BIRLA CENTRAL LIBRARY
PILANI (RAJASTHAN)

Call No. 665.5
D926
v.4

Accession No 31146

THE
SCIENCE OF PETROLEUM

VOLUME IV

THE SCIENCE OF PETROLEUM

A COMPREHENSIVE TREATISE OF THE PRINCIPLES AND PRACTICE OF THE PRODUCTION REFINING TRANSPORT AND DISTRIBUTION OF MINERAL OIL

DR. A. E. DUNSTAN
CHIEF CHEMIST OF THE ANGLO-IRANIAN OIL COMPANY, LTD.
LONDON
Managing Editor

PROFESSOR A. W. NASH
HEAD OF THE DEPARTMENT OF OIL ENGINEERING AND REFINING
THE UNIVERSITY, BIRMINGHAM, ENGLAND
Editor of Contributions

DR. BENJAMIN T. BROOKS
CONSULTING CHEMICAL ENGINEER, NEW YORK
Editor for the United States of America

SIR HENRY TIZARD, K.C.B., F.R.S.
RECTOR OF THE IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY
LONDON
Consulting Editor

VOLUME IV

OXFORD UNIVERSITY PRESS
LONDON NEW YORK TORONTO
1938

OXFORD UNIVERSITY PRESS
AMEN HOUSE, E.C. 4
LONDON EDINBURGH GLASGOW NEW YORK
TORONTO MELBOURNE CAPETOWN BOMBAY
CALCUTTA MADRAS
HUMPHREY MILFORD
PUBLISHER TO THE UNIVERSITY

PRINTED IN GREAT BRITAIN

CONTENTS

VOLUME I

PART I

ORIGIN AND PRODUCTION OF CRUDE PETROLEUM

Sections 1–17

VOLUME II

PART II

CHEMICAL AND PHYSICAL PRINCIPLES OF THE REFINING OF MINERAL OILS

Sections 18–39

OXIDATION AND OXY-COMPOUNDS

SULPHUR COMPOUNDS

NITROGEN COMPOUNDS

INORGANIC CONSTITUENTS OF PETROLEUM

COLLOIDICS

VISCOSITY

DENSITY AND REFRACTIVE INDEX

SPECTROGRAPHIC AND X-RAY APPLICATION

OPTICAL PROPERTIES

THERMAL, CRITICAL, AND P-V-T. DATA AND THEIR MEASUREMENT

PHYSICAL PROPERTIES AND MOLECULAR STRUCTURE

VOLUME III

PART II (*continued*)

CONDENSER, HEAT EXCHANGE, AND TUBE-HEATER EQUIPMENT

INSULATION

VOLUME IV

PART III

UTILIZATION OF MINERAL OILS AND THEIR DERIVATIVES

Section 40

MOTOR SPIRITS, SOLVENTS, DIESEL FUELS, ETC.

OIL FUEL

LUBRICANTS

Synthetic Lubricants

WAXES

ASPHALTIC BITUMEN, COKE, AND REFINERY RESIDUES

SYNTHETIC DERIVATIVES FROM PETROLEUM

Chlorinated Compounds and Derivatives

Alcohols

SPECIAL PRODUCTS

PART IV

DETONATION AND COMBUSTION

Sections 41 and 42

SLOW OXIDATION

IGNITION

FLAME PROPAGATION AND DETONATION

SPECIFIC BEHAVIOUR OF FUELS AND DOPES

METHODS OF KNOCK RATING

ENGINE ASPECTS

PART V

BITUMINOUS MATERIALS AND THEIR PRODUCTS

Sections 43 and 44

PART III

UTILIZATION OF MINERAL OILS AND THEIR DERIVATIVES

SECTION 40

IV B

SECTION 40

PRODUCTS OF PETROLEUM

MOTOR SPIRITS, SOLVENTS, DIESEL FUELS, ETC.	
Introduction	F. H. GARNER
Motor Fuels in the United States	J. G. DETWILER and M. P. DOSS
Motor Fuels in European Countries	F. H. GARNER and E. W. HARDIMAN
Natural Gasoline	G. GRANGER BROWN and D. L. KATZ
Aviation Fuels	R. HASKELL
British Practice in Regard to Aviation Fuels	F. R. BANKS
Aviation Fuels—French Practice	P. DUMANOIS
Special Engine Fuels	D. A. HOWES
Industrial Petroleum Solvents and White Spirits	F. N. HARRAP
Petroleum as a Source of Lacquer Solvents	T. H. DURRANS
Kerosine	J. KEWLEY and C. L. GILBERT
Light Diesel Fuels	G. D. BOERLAGE and J. J. BROEZE
Diesel Fuel	L. J. LE MESURIER
Oil Gas	L. J. WILLIEN
The Evaluation of Oils for Gas Making—English Practice	R. H. GRIFFITH
OIL FUEL.	
The Industrial Application of Fuel Oils, including Burner Practice	I. LUBBOCK, F. J. BATTERSHILL, and R. H. B. FORSTER
Utilization of Fuel Oils for Steam-raising Purposes	J. S. S. BRAME
Coal-in-Oil Suspensions	A. B. MANNING
LUBRICANTS.	
Lubrication—Introductory	D. R. PYE
Chemical and Physical Forces in Lubrication	G. L. CLARK, R. R. STERRETT, and B. H. LINCOLN
The Chemical Nature of Lubricating Oils	F. B. THOLE
Density, Refractive Index, and Related Characteristics of Lubricating Oils and Bituminous Substances	A. L. WARD, S. S. KURTZ, JR., and W. H. FULWEILER
Lubricating Grease	F. MACKLEY
Apiezon Oils	C. R. BURCH
The Use of Anti-oxidants in Lubricating Oils	D. A. HOWES
Extreme Pressure Lubricants	H. C. MOUGEY
The Practical Selection of Improved Lubricants	L. L. DAVIS, B. H. LINCOLN, and B. E. SIBLEY
Mechanical Testing of Lubricants—Laboratory Engines and Work Factor Methods	G. M. MAVERICK and A. J. BLACKWOOD
Engine Tests of Lubricants	C. H. BARTON and O. THORNYCROFT
The Lubrication of Internal-combustion Engines	D. R. PYE
Lubrication Practice	S. J. M. AULD
Metal Working Oils	P. BEUERLEIN

CONTENTS TO SECTION 40 (*cont.*)

MOTOR SPIRITS, SOLVENTS, DIESEL FUELS, ETC.

INTRODUCTION

By **F. H. GARNER, Ph.D., F.I.C., M.I.A.E.**

Anglo-American Oil Company, Ltd.

Of the primary products of petroleum—gasolines, kerosines, Diesel fuel, fuel oils, lubricating oils, and asphalts—the first four only are considered in this section, and lubricating oils and asphalts are more conveniently included elsewhere in this treatise.

The following tables show the quantities in thousands of barrels of motor fuel, kerosine, gas and fuel oil, lubricants, and miscellaneous totals for the years 1933–6 togetner with the consumptions in the more important countries of the world for 1936 [5, 1936–7].

Table I

World Consumption of Petroleum Products 1933–6

Thousands of Barrels

Year	*Motor fuel*	*Kerosine*	*Gas and fuel oil*	*Lubricants*	*Misc.*	*Total*
1933	536,684	110,659	552,846	41,552	165,182	1,406,923
1934	586,126	120,134	602,292	43,829	154,818	1,507,599
1935	620,092	124,442	651,382	46,902	171,657	1,614,475
1936	674,825	129,930	707,920	51,215	193,890	1,757,780

With the exception of asphalts and paraffin wax, all petroleum products are used mainly either as fuel or as lubricants; the fuel may be subdivided into that used for internal-combustion engines (spark or compression ignition) and for external combustion, and these tables show that gas and fuel oil is consumed in larger quantities than motor fuel. At the same time, in such important consuming countries as the U.S.A., the United Kingdom, France, Canada, and Germany, the consumption of motor fuel is larger than that of gas and fuel oil. The tables supplement the data given in articles on gasolines in the U.S.A. and in other countries.

Gasolines.

In the article 'Motor Fuels in the United States', p. 2395, the relation between specifications of gasoline and the behaviour in the internal-combustion engine is discussed and the same general conclusions naturally apply to fuels marketed in other countries. It can be stated that the quality of gasoline marketed throughout the world has attained a considerable degree of uniformity, but more volatile gasolines are, naturally, marketed in the coldest countries, such as Finland, to ensure easy starting and good warming-up properties, whereas in the tropical countries products are of somewhat lower volatility and lower Reid vapour pressure in order to minimize the possibility of vapour lock and losses in storage. The octane number also varies to some extent, but not very widely, and indeed in some individual countries where three grades are marketed the range of octane numbers is almost as great as that normally found with reputable brands of gasoline throughout the world.

Gasoline is also, unfortunately, an important product from the point of view of taxation, and definitions adopted for fiscal purposes vary very widely, as would be expected, since the only satisfactory definition is one based on use, and special products such as gasoline, kerosine, and Diesel fuel overlap to such an extent that no definition based on specific gravity or distillation range can be entirely satisfactory. The history of all such fiscal definitions has been that a cheaper product such as kerosine is used as a substitute for gasoline, and additional regulations outside the fiscal definition have had to be adopted in order to prevent such use or the mixing of the cheaper product with the more highly taxed product. In certain countries even gas oil has been used as a fuel for gasoline engines, for which purpose it is entirely unsuitable, and, in consequence, serious difficulties have been met through dilution and incomplete combustion.

Table II

World Consumption of Petroleum Products by Countries, 1936

Thousands of Barrels

	Motor fuel	*Kerosine*	*Gas and fuel oil*	*Lubricants*	*Misc.*	*Total*
United States .	482,000	50,000	405,000	22,500	130,500	1,090,000
Russia . . .	14,800	30,400	63,200	8,500	17,800	134,700
United Kingdom .	38,500	6,400	27,000	2,900	4,100	78.900
France . . .	23,000	1,490	13,000	1,640	3,200	42,330
Canada . .	17,500	1,990	15,600	1,060	2,000	38,150
Germany . .	17,000	990	12,200	4,020	2,900	37,110
Japan . . .	8,100	1,500	14,750	1,900	1,900	28,150
Argentina . .	6,200	1,320	16,400	450	890	25,260
Italy . . .	4,500	1,480	11,000	720	2,200	19,900
Mexico . .	2,540	620	11,500	170	2,500	17,330
Roumania . .	790	1,240	11,700	220	2,000	15,950
Neth. West Indies .	180	30	13,200	35	3,820	17,265
British India . .	2,480	6,500	3,800	990	1,300	15,070
Australia . .	6,800	1,170	3,340	460	670	12,440
Neth. East Indies .	1,490	2,000	5,100	160	1,240	9,990
Netherlands . .	3,480	1,830	2,400	380	890	8,980
Venezuela . .	590	30	1,200	35	5,900	7,755
Sweden . .	3,480	890	2,150	360	600	7,480
China . . .	990	2,460	2,800	260	340	6,850
Brazil . . .	2,510	750	3,280	180	70	6,790
Spain . . .	2,800	190	1,650	100	210	4,950
Iran . . .	430	980	3,200	200	1,500	6,310
Egypt . . .	540	2,000	2,890	180	190	5,800
South Africa . .	3,100	570	1,140	200	200	8,210
Denmark . .	2,200	560	1,640	160	290	4,850
Belgium . .	2,520	210	1,190	220	420	4,560
Cuba . . .	490	70	3,750	40	110	4,460
Trinidad . .	105	70	3,800	30	290	4,295
Philippine Islands .	1,000	580	2,400	80	130	4,190
Norway . .	1,190	305	1,980	95	110	3,680
Switzerland . .	1,830	190	1,150	160	40	3,370
Chile . . .	650	60	2,750	75	40	3,575
New Zealand .	1,190	160	1,240	80	115	3,585
Poland . . .	970	1,010	600	400	300	3,280
Czechoslovakia .	1,880	440	740	220	180	3,380
Iraq . . .	310	220	2,080	55	690	3,355
British Malay .	580	320	2,060	70	190	3,220
Hawaiian Islands .	980	140	1,990	65	70	3,245
Austria . .	910	290	1,200	145	140	2,685
Panama Canal Zone	110	30	2,300	20	40	2,500
Uruguay . .	630	60	1,800	40	40	2,570
Algeria . .	1,300	400	340	110	130	2,280
Irish Free State .	1,110	520	260	70	200	2,160
Peru . . .	420	430	760	60	300	1,970
Greece . . .	370	150	1,060	60	50	1,690
Porto Rico . .	490	70	990	35	40	1,625
Portugal . .	600	410	440	40	60	1,550
Hungary . .	420	400	450	90	100	1,460
Finland . .	580	360	140	95	95	1,270
French Morocco .	770	95	110	40	130	1,145
Others . .	6,700	5,550	23,200	1,040	2,670	39,160

Kerosine.

It is often assumed that the consumption of kerosines is steadily declining, and whilst this is true as regards the use of kerosine in wick-fed lamps for illumination purposes, there has been a considerable increase in the use of motor kerosine as a fuel for internal-combustion engines, and over all for the years 1933 to 1936 there has been a slight increase in the world consumption. Whilst the use of kerosine for motive purposes, light, and power generation has undoubtedly been stimulated by the taxation of gasoline, kerosine has been used in internal-combustion engines for a long period of time: it was the knocking of kerosine in small engines used for lighting sets that drew the attention of Kettering to the problem and led to the work of Midgley, culminating in the discovery in 1921 of lead tetraethyl. The motor kerosine or power vaporizing oil marketed for use in such engines has to meet a relatively high octane number and volatility, and thus the essential demands for kerosine for power purposes are fundamentally different from those for illuminating purposes. It will be noted that in the case of gasoline and motor kerosine a product of high octane number, that is, of naphthenic, aromatic, or branched-chain structure, is required, whereas for illuminating oil, and Diesel fuel for high-speed engines, a paraffinic structure of the straight-chain type is preferred.

Liquefied Petroleum Gases.

A feature of the last 5 or 6 years has been the development of liquefied petroleum gases, the increase on the American market being from 4·5 million gallons in 1928 to over 48 million gallons in 1934 [3, 1935]. These gases consist principally of propane and butane, and the most important use for the butane is in the domestic field, whereas the principal use of the propane is in the industrial field. Liquefied gases are, of course, derived from natural gas and refinery gas.

Gas Oil, Diesel Fuel, and Fuel Oil.

Gas oil was the name originally applied to the product used in gas-works for the carburetting of water gas, but in recent years the use of gas oil for high-speed compression-ignition engines has assumed increasing importance, and for this purpose it is usually described as light Diesel fuel, or light Diesel fuel oil. Diesel fuels for stationary and marine engines may be either distillates of higher viscosity than those required for road transport or blends of distillates with suitable petroleum residues. Fuel oils for domestic burner installations are usually distillate oils, but for the larger heating installations, or industrial use, either residual fuels or blends of such fuels with distillates are used. It has been found necessary, in most countries, to market fuel oils in a range of differing viscosities to meet the requirements of different fuel-oil burner installations according to the type of burner and preheating available, either in preheaters, or in storage tanks.

It is somewhat difficult to obtain figures for the quantities of fuel oils used in different industries, but the following table will show the approximate quantities used under the various headings in the U.S.A. during 1934 [4, 1935]:

	bbl.
High-speed Diesel oil	about 1×10^6
Army and Navy	8×10^6
Ships, oil-burning and Diesel . . .	69×10^6
Railways	53×10^6
Industrial	52×10^6
Refinery	47×10^6
Distillate (oil-burner installations) . .	$49–54 \times 10^6$

In the United States the development of high-speed Diesel engines for road transport was later than in many European countries, where the high-speed Diesel engine has largely replaced the gasoline engine for heavy-duty commercial vehicles and buses. The rapid development of high-speed Diesel engines is shown in Fig. 1 [7, 1536] giving the number of high-speed Diesel engines in use in transport for Italy, France, Germany, and the United Kingdom over the 5 years 1932–7. Although this development has been quite rapid, it is largely confined to heavy-duty commercial service which represents only a small proportion of the total, since even for commercial work the bulk of the traffic engaged consists of relatively light-duty vehicles. For the United Kingdom for 1935/1936 the proportionate consumption of high-speed Diesel fuel for transport to gasoline was 2½%, but higher figures than this are attained in continental countries, notably France and Germany.

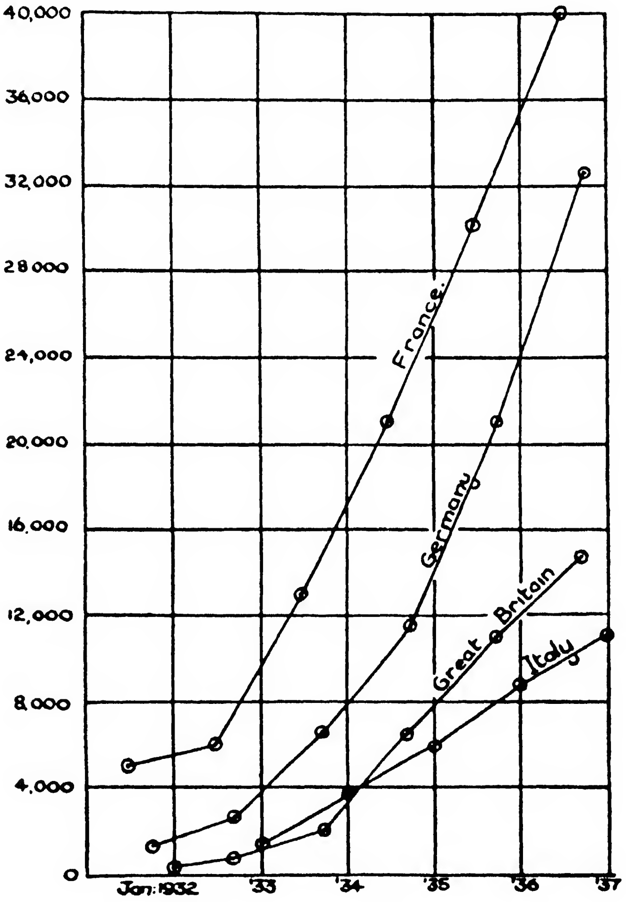


FIG. 1. Diesel engined vehicles.

For marine operation the feature of recent years has been the advance in motor-driven vessels as compared with oil-fired vessels, and the two Tables III and IV summarize this tendency. These figures are from the report of *Lloyd's Register for Shipping* for the year 1935–6 and show in Table III the proportionate tonnage built over the period 1918–36 distributed between coal-fired, oil-fired, and motor-driven [6]. It should be noted that the figures in Tables III and IV under the heading of oil-fired vessels are steamers *fitted* for burning oil, but it is not claimed that such vessels always use oil fuel.

The second table (IV) shows all existing vessels of 100 tons and upwards for the period 1933–7, and shows the remarkable relative increase in the Diesel-engined vessels during these years.

TABLE III

Table showing Tonnage of Coal- and Oil-fired Vessels, and Motor-driven Vessels built between 1918 and 1935. (Built to class on 'Lloyd's Register')

	Tons gross		
Year	*Coal-fired*	*Oil-fired*	*Fitted with internal-combustion engines including Diesel engines*
1918–19	2,491,213	1,193,659	75,934
1919–20	2,111,289	1,995,788	79,805
1920–1	1,260,465	1,867,115	101,608
1921–2	895,032	1,395,929	226,552
1922–3	662,565	782,830	165,229
1923–4	468,153	242,162	164,336
1924–5	671,405	337,411	302,461
1925–6	418,503	303,835	602,451
1926–7	297,948	275,889	393,225
1927–8	631,240	431,391	812,437
1928–9	600,270	351,113	786,353
1929–30	680,699	276,144	847,403
1930–1	318,107	203,457	1,212,525
1931–2	57,120	259,897	598,247
1932–3	110,959	148,171	188,020
1933–4	89,373	14,927	243,897
1934–5	150,445	49,695	552,060
1935–6	198,976	222,420	580,410

Lubricating Oil.

In Table I figures were given for the total consumption in various countries for the year 1936, and it is of interest to analyse these data from the point of view of the relative quantities of lubricants to motor fuel, gas and fuel oil, practically all of which represents petroleum products consumed in the development of power. In this connexion, the figure for ratio of lubricating oil to gasoline used in motor vehicles was formerly taken as being in the neighbourhood of 6%, but the figure applicable at the present time is stated to be 1·5%. The following table (V) shows the percentage of lubricants to the combined gasoline, gas and fuel oil consumption for various countries in 1933–6.

TABLE IV

Table embracing all existing Vessels of 100 Tons and upwards, as recorded in 'Lloyd's Register'

Year	*Coal-fired*	*Oil-fired*	*Motor-driven*
1922–3	45,338,327	14,464,162	1,540,463
1923–4	44,876,570	15,792,418	1,666,385
1924–5	42,384,270	17,154,072	1,975,798
1925–6	41,862,181	17,804,122	2,714,073
1926–7	40,935,114	18,243,539	3,493,284
1927–8	40,514,719	18,481,759	4,270,824
1928–9	40,674,097	19,053,014	5,432,302
1929–30	40,358,396	19,420,895	6,628,102
1930–1	40,069,679	19,857,788	8,096,337
1931–2	39,289,061	20,002,307	9,431,433
1932–3	38,194,758	20,135,006	10,038,377
1933–4	36,373,859	20,053,273	10,200,392
1934–5	33,895,555	19,857,711	10,604,526
1935–6	32,537,556	19,885,070	11,304,691
1936–7	31,947,618	19,766,668	12,290,599

Of the total of 51,714,286 tons oil- and coal-fired vessels in 1936–7, 42,605,474 tons were fitted with steam-reciprocating engines and 9,108,812 tons with steam turbines (including turbo-electric).

A proportion of the lubricating oil will be used for the lubrication of machinery for which power is generated from coal or by water, but it is interesting to note that the overall figure is in the neighbourhood of 3·7%. The proportion, however, varies considerably with different countries, presumably according to the relative importance of petroleum as against other methods of generating power, from a figure of approximately 2·5% in the United States to the more recent figure for Germany of 13·77%. The use of vegetable oils as lubricants in some countries is also an important factor.

TABLE V

Percentage Lubricants to combined·Motor Fuel, Gas and Fuel Oil

Country	*1936*	*1935*	*1934*	*1933*
U.S.A. . . .	2·53	2·44	2·50	2·47
Russia	10·90	11·12	11·60	11·55
United Kingdom . .	4·43	4·28	4·74	5·27
France . . .	4·56	4·67	6·19	5·95
Canada . . .	3·20	3·21	2·64	2·65
Germany . . .	13·77	13·83	10·67	10·10
Italy	4·64	4·79	5·29	5·58
Total . . .	3·71	3·70	3·80	3·81

Price of Petroleum Products.

The following table shows the decline in gasoline cost over a period of years in the United States, and this has been effected by economies in refining (thus the loss on the crude in 1920 was 4·3% as against 1·8% in 1934), although the product has been considerably improved in every respect, notably in ease of starting, warming up, and acceleration, together with improved octane number. However, during this period of years the tax cost in the United States has increased tremendously, with the result that the reduction in cost of manufacture which has been effected by the refiner has not been passed on to the consumer [2, 1935].

TABLE VI

Decline in Fuel Cost per Car (based on an average of 600 gallons per year)

Year	*Cost of gasoline*	*Tax cost*	*Total cost*
	$	$	$
1920 . .	178.44	0.54	178.98
1921 . .	156.66	1.20	157.86
1922 . .	148.97	2.28	151.25
1923 . .	126.36	5.46	131.82
1924 . .	116.76	8.80	125.56
1925 . .	120.54	12.66	133.20
1926 . .	125.54	14.46	140.00
1927 . .	109.68	16.86	126.54
1928 . .	107.40	18.24	125.64
1929 . .	107·52	21.00	128.52
1930 . .	96.96	22.74	119.70
1931 . .	77.88	24.00	101.88
1932 . .	79.80	27.78	107.58
1933 . .	77.46	32.46	109.92
1934 . .	81.84	31.20	113.04

This table bears reference to the U.S.A., but the following figures will show the wide variation in price of gasoline in different countries showing the importance of tax in determining the price to the consumer since the basic price for the gasoline is the same in all cases [1, 1937]:

ling Station Prices of Gasoline, Kerosine, and Lubrica-g Oil in Various Countries, Jauuary, 1937. (Includes Taxes and Duty)

ces quoted are those in the capital city of each country, in cents per U.S. gallon

Country	*Gasoline*	*Kerosine*		*Lubricating oil*
		Lamp	*Power*	
gentina	26·1	19·3	15·9	111
stralia	28·5	24·4	14·2	122
lgium	27·0*	29·0	..	141
nada	19·6	12·5	..	133
ance	40·6	35·2	..	174
rmany	59·6	53·4	..	290
lland	30·0	17·6	..	176
ly	48·0	42·0	40·0	159
pan	17·1	17·3	13·3	102
uth Africa	26·9	15·2	14·3	161
eden	23·8	15·2*	11·4*	180
itzerland	37·5	22·7	14·7	157
nited Kingdom	30·6	24·7	..	140
nited States	18·5	12·0	..	100

* Price in tins.

The reduction in cost of the greatly improved gasoline far exceeds the reduction in cost of the raw material as shown by the following table [2, 1935]:

TABLE VII

Comparison of Crude-oil and Wholesale Gasoline Prices

	1919	*1934*	*Decline %*
Pennsylvania:	$	$	
Crude	4.14	2.43	41·30
Gasoline	0.1960	0.0672	65·71
Oklahoma:			
Crude	2.118	1.020	51·84
Gasoline	0.1730	0.0475	72·54
California:			
Crude	1.4094	0.9200	34·72
Gasoline	0.1516	0.0819	45·98

REFERENCES

World Retail Prices. U.S. Bur. of Mines. **6** (1) 1937.
American Petroleum Industry, 1935 (A.P.I.), pp. 78–9.
American Petroleum Industry, 1935 (A.P.I.), p. 120.
American Petroleum Industry, 1935 (A.P.I.), pp. 121–6.
5. GARFIAS, V. R., and WHETSEL, R. V. *Petroleum Times*, **35** (896), 346 (1936); ibid. **37** (945), 249 (1937).
6. *Lloyd's Register of Shipping.*
7. SPRAKE, C. H. *Petroleum Technology in 1936* (*J.I.P.T.*) p. 154.

MOTOR FUELS IN THE UNITED STATES

By **J. G. DETWILER**, B.Sc., F.C.S., *Technologist*, and **M. P. DOSS**, *Technical Librarian*,
The Texas Company

THE history of the gasoline industry in the United States is also that of the automobile industry, for it was only due to the invention and commercial application of the internal-combustion engine that gasoline became a valuable refinery product, no longer a waste material the disposal of which was a real problem. From 1910 on, gasoline became a product of increasing importance, and in 1915 the amount of gasoline produced exceeded that of kerosine. In Fig. 1 are shown curves for passenger cars and truck production for the period 1895–1934; in Fig. 2 gasoline versus kerosine production in the United States for the period 1900–34. In the year 1934 the total motor-fuel consumption was 16,595,180,000 gal., which was the second largest in history according to the American Petroleum Institute's Department of Statistics. This consumption had been exceeded only in 1931, when the total consumption was 16,719,239,000 gal. The consumption by States for 1934 and the corresponding car registration and consumption per car are shown in the attached table. The average consumption for motor vehicles including trucks in this country is 610 gal. of gasoline annually. Fig. 3 shows the ratio of straight-run to cracked and natural gasoline produced. The gasoline marketed in the United States at present falls mainly into three grades—premium grade, which is a product similar in anti-knock rating to ethyl gasoline, having an anti-knock rating of 76 octane units; the ordinary grade averaging 70 octane units, and the third-grade gasoline which in most parts of the country does not meet any octane standard, but has a volatility range within U.S. Motor Fuel Specifications VV. G. 101 of the Federal Specifications Board, issued 21 July 1931 (see Fig. 7).

Specifications of U.S. Navy and Federal Specifications Board

So long as the gasoline demand was limited and no difficulty was experienced with the mechanical side of the automobile that could be attributed to the fuel, no particular attention was paid to specifications for the fuel other than that most car manufacturers insisted on a light Baumé gravity. In some cases it was claimed that 76° Bé. gasoline was necessary, and the first Government specification issued by the Navy Department in 1907 (no. 24 G. 5) called for only 'a high grade refined gasoline free from all impurities', having a gravity of 70° Bé., and requiring that it should leave no residue after 1 hour's evaporation in an open platinum dish in boiling water. This last requirement was in no sense a definite distillation test, but was included to ensure the absence of kerosine or lubricating oil.

While the trade in general continued for a number of years to consider gravity the sole criterion of quality, the Navy Department in its temporary specification 8 G. 1, issued 6 April 1910, made no mention of gravity, but gave the distillation range as follows:

Initial boiling-point .	below 135° F.
10%	„ 150° F.
50%	„ 200° F.
100%	„ 310° F.
Recovery . .	above 96% minimum

and also the requirement that 5 c.c. of the product poured

TABLE I

State	*Total gasoline consumption in United States 1934*	*Automobile registration by States 31 Dec. 1934*	*Gasoline consumption per car*
Alabama	155,047,000	225,732*	687
Arizona	73,219,000	96,586	758
Arkansas	140,156,000	198,091	708
California	1,334,177,000	2,006,255	665
Colorado	172,756,000	274,231	630
Connecticut	254,933,000	357,787	713
Delaware	41,556,000	54,240	766
District of Columbia	103,734,000	163,070	636
Florida	236,775,000	335,205	706
Georgia	239,498,000	376,993	635
Idaho	65,770,000	108,863	604
Illinois	1,025,918,000	1,456,241	704
Indiana	465,438,000	803,271	579
Iowa	403,803,000	666,440	606
Kansas	378,781,000	528,664	716
Kentucky	184,367,000	332,177	555
Louisiana	178,457,000	244,007	731
Maine	116,993,000	178,995	654
Maryland	206,279,000	332,892	620
Massachusetts	587,789,000	785,392	748
Michigan	781,971,000	1,148,953	681
Minnesota	431,545,000	697,672	619
Mississippi	131,263,000	174,934	750
Missouri	489,401,000	739,813	662
Montana	85,484,000	128,336	666
Nebraska	223,372,000	406,632	549
Nevada	24,707,000	32,230	767
New Hampshire	70,640,000	113,134	624
New Jersey	734,521,000	864,641	850
New Mexico	56,154,000	82,900	677
New York	1,577,019,000	2,269,355	695
North Carolina	279,796,000	439,351	637
North Dakota	102,931,000	156,203	659
Ohio	955,470,000	1,613,265	592
Oklahoma	300,431,000	477,292	629
Oregon	165,978,000	274,117	606
Pennsylvania	1,136,344,000	1,681,202	676
Rhode Island	108,864,000	142,394	765
South Carolina	132,347,000	202,834	652
South Dakota	109,514,000	169,975	644
Tennessee	212,037,000	336,313	630
Texas	875,034,000	1,312,152†	667
Utah	64,140,000	101,926	629
Vermont	48,550,000	77,921	623
Virginia	259,123,000	373,908‡	693
Washington	260,778,000	422,238	618
West Virginia	147,609,000	194,231§	760
Wisconsin	420,725,000	709,359	593
Wyoming	43,986,000	64,990	677
Total	16,595,180,000	..	..

Figures are in gallons. * 30 Sept. 1934.

† For 15-month period ending 31 March 1935; date changed from 31 Dec.

‡ For year ended 31 March 1935. § For 6-month period.

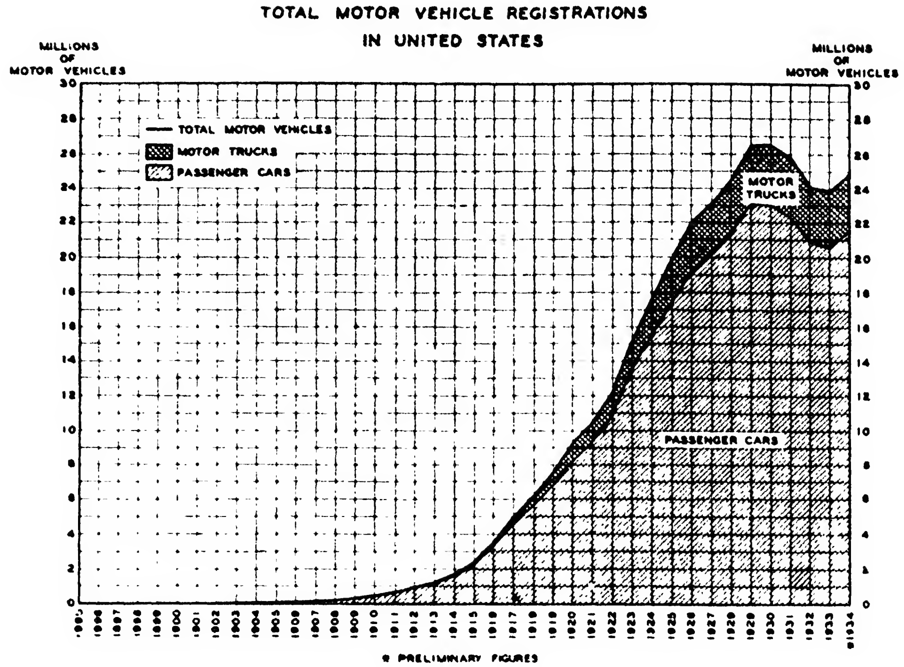


FIG. 1.

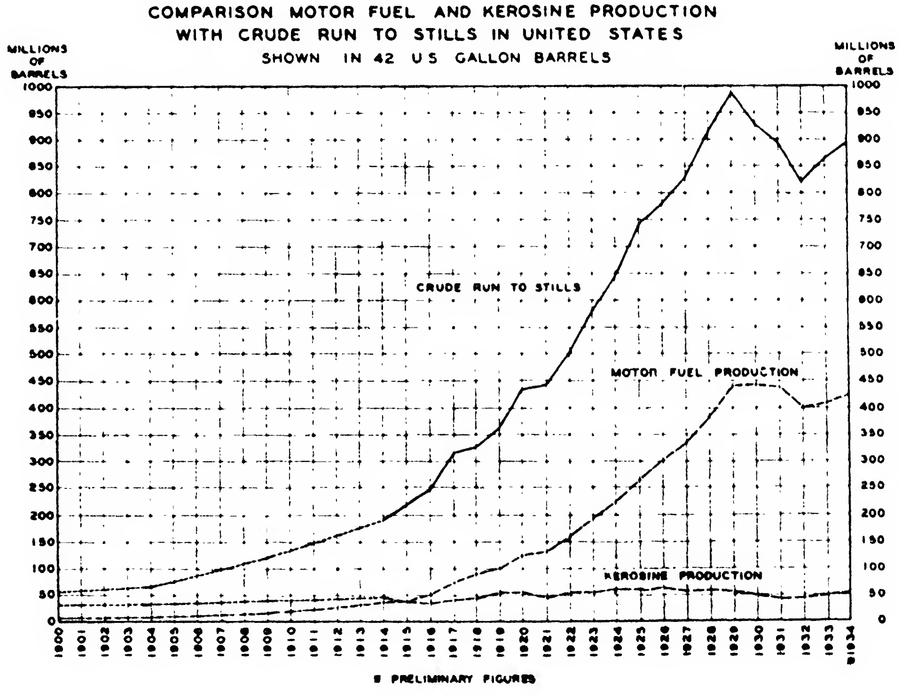


FIG. 2.

on white paper should evaporate completely without leaving any stain. This specification was issued officially on 1 August 1910, the distillation being changed to:

Initial boiling-point .	not higher than 180° F.
50%	below 230° F.
100% . . .	„ 310° F.
Recovery . . .	above 98%, minimum

NOTE: The official specification curiously enough calls for an I.B.P. *not lower than 180° F.* which was evidently an error.

This specification is identical with M. 89 of the War Department issued 26 August 1913. On 1 June 1912 contracts for 1913 Navy supplies called for:

Initial boiling-point .	below 145° F.
50%	„ 250° F.
95%	„ 315° F.
100%	„ 330° F.
Recovery . . .	98%, minimum

which was later made official under Specification 8 G. 1 A allowing a less volatile product.

Initial boiling-point	'not lower than' 130° F.
50%	below 275° F.
95%	„ 340° F.
100%	„ 360° F.
Recovery	98%, minimum

The next change was in 1917, the Navy contract covering 1917 requirements calling for a still less volatile product.

Initial boiling-point	below 140° F.
End-point	„ 375° F.

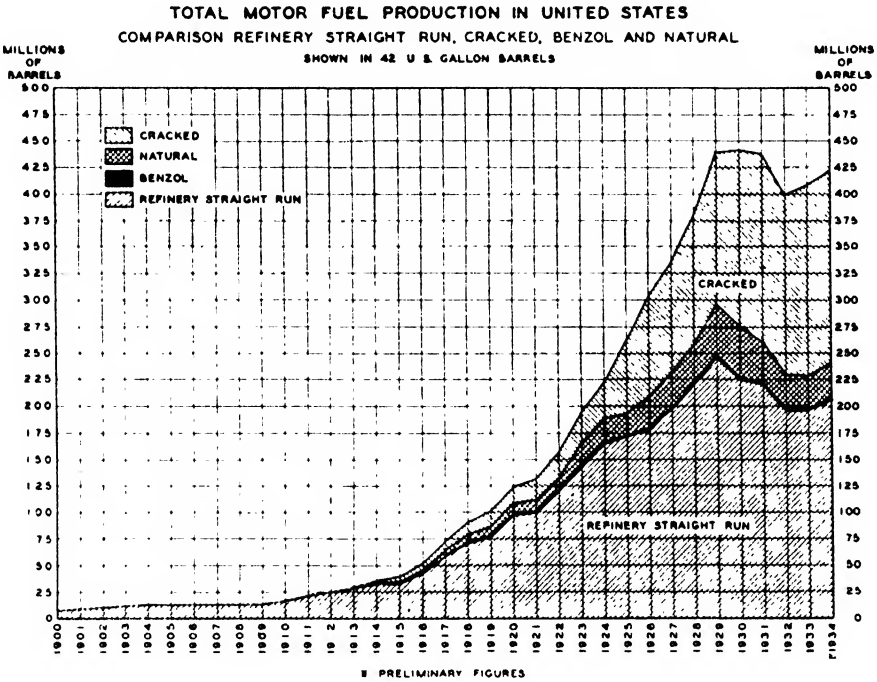


Fig. 3.

However, Specification 8 G. 1B of September 1917 required a more detailed distillation test and a less volatile gasoline, as follows:

Initial boiling-point	not above 140° F.
20%	below 221° F.
45%	„ 275° F.
90%	„ 356° F.
End-point	„ 428° F.
Recovery	95%, minimum

A vapour tension of not greater than 10 lb. per sq. in. at 100° F. was also specified, and the same specification was issued later by the War Department as no. 3529 in July 1919.

Due to the urgent necessity of having uniform specifications for petroleum products to be used by the Government departments during the World War, President Wilson on 31 July 1918 directed the organization of the Committee on Standardization of Petroleum Specifications. The first specification covering motor gasoline prepared by this committee and adopted on 2 October 1918 was the same as Navy 8 G. 1B given above. This specification was revised on 25 November 1919, the 45% point being replaced by the 56% (284° F.), the 90% raised to 374° F., and the end-point to 437° F. Detailed instructions covering the distillation test were also given for the first time, these being the modified A.S.T.M. procedure. This specification was in effect for a number of years, a colour and corrosion requirement being added in 1922. In that same year the distillation range was altered to the following:

Initial boiling-point	below 131° F.
20%	„ 221° F.
50%	„ 284° F.
90%	„ 392° F.
End-point	„ 437° F.
Recovery	95%, minimum

In 1924 a sulphur requirement of 0·10% maximum was appended and the corrosion test made more stringent. In 1929 the U.S. Motor Gasoline specification was broadened to cover two products, first, Specification 622*a*—U.S. Motor Gasoline:

10%	122–76° F.
50%	below 284° F.
90%	„ 392° F.
End-point	„ 437° F.
Recovery	95%, minimum

The requirement was also made that for each per cent. distillation loss less than 4 the minimum 10% temperature requirement should be lowered 5·4°. Furthermore, for tropical storage the minimum 10% reading could be raised to 140° F.

The other motor fuel designated as Motor Fuel V had the following distillation:

10%	122–49° F.
50%	below 257° F.
90%	„ 356° F.
End-point	„ 401° F.
Recovery	95%, minimum

In 1931 the 10% reading on U.S. Motor Gasoline was changed to 167° F., maximum, evaporated, and the end-point requirement eliminated, recovery reading also being changed to 2% maximum residue. A vapour-tension requirement was included of 12 lb. (8 lb. in tropical areas) at 100° F. Similar changes were made in specifications for Motor Fuel V, the 10% now reading 158° F. maximum evaporated, end-point eliminated, and vapour pressure of 10 lb. at 100° F. added. Figs. 4–7 show the trend in Government specifications since 1910.

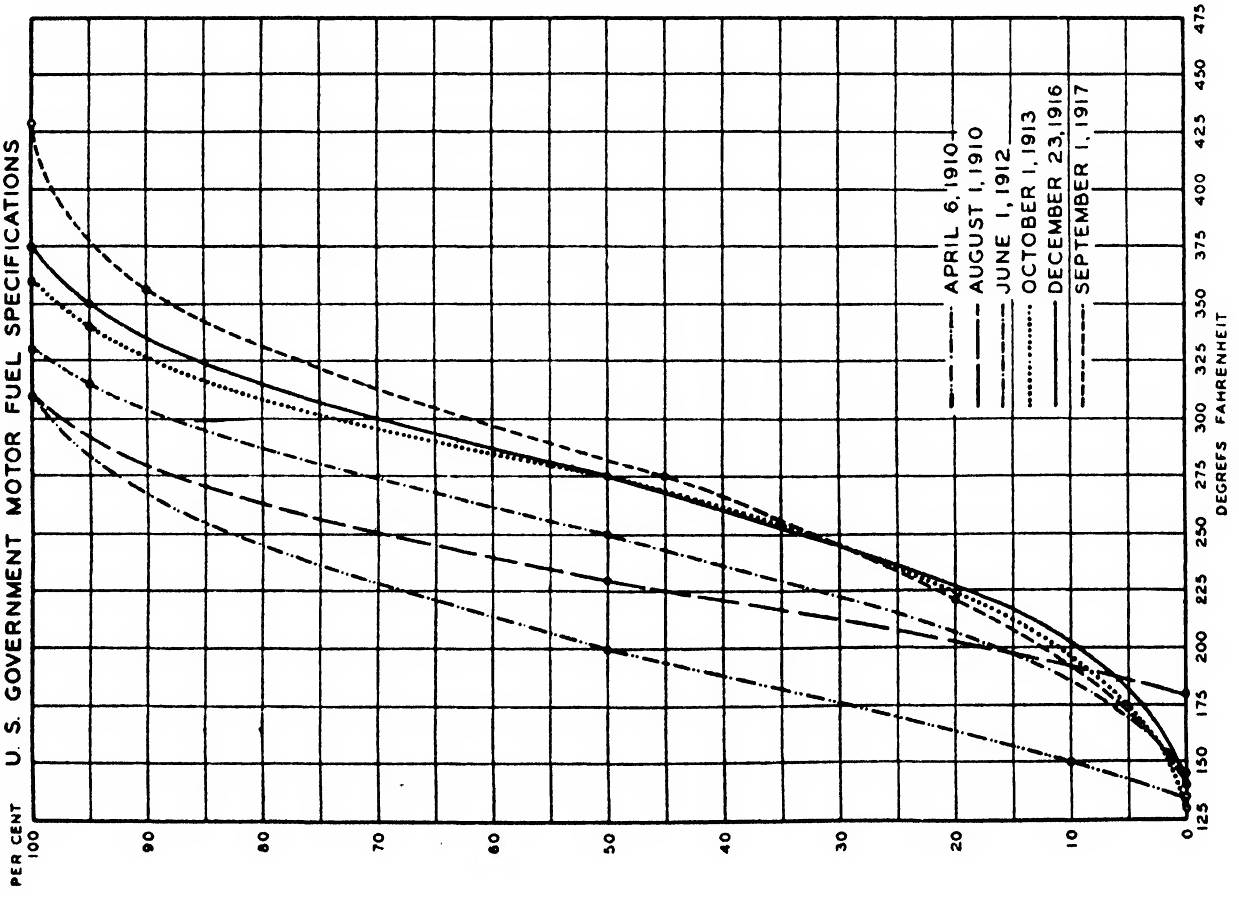

U. S. GOVERNMENT MOTOR FUEL SPECIFICATIONS
PER CENT
100
90
80
70
60
50
40
30
20
10
0
125
150
175
200
225
250
275
300
325
350
375
400
425
450
475
DEGREES FAHRENHEIT
APRIL 6, 1910
AUGUST 1, 1910
JUNE 1, 1912
OCTOBER 1, 1913
DECEMBER 23, 1916
SEPTEMBER 1, 1917

FIG. 4.

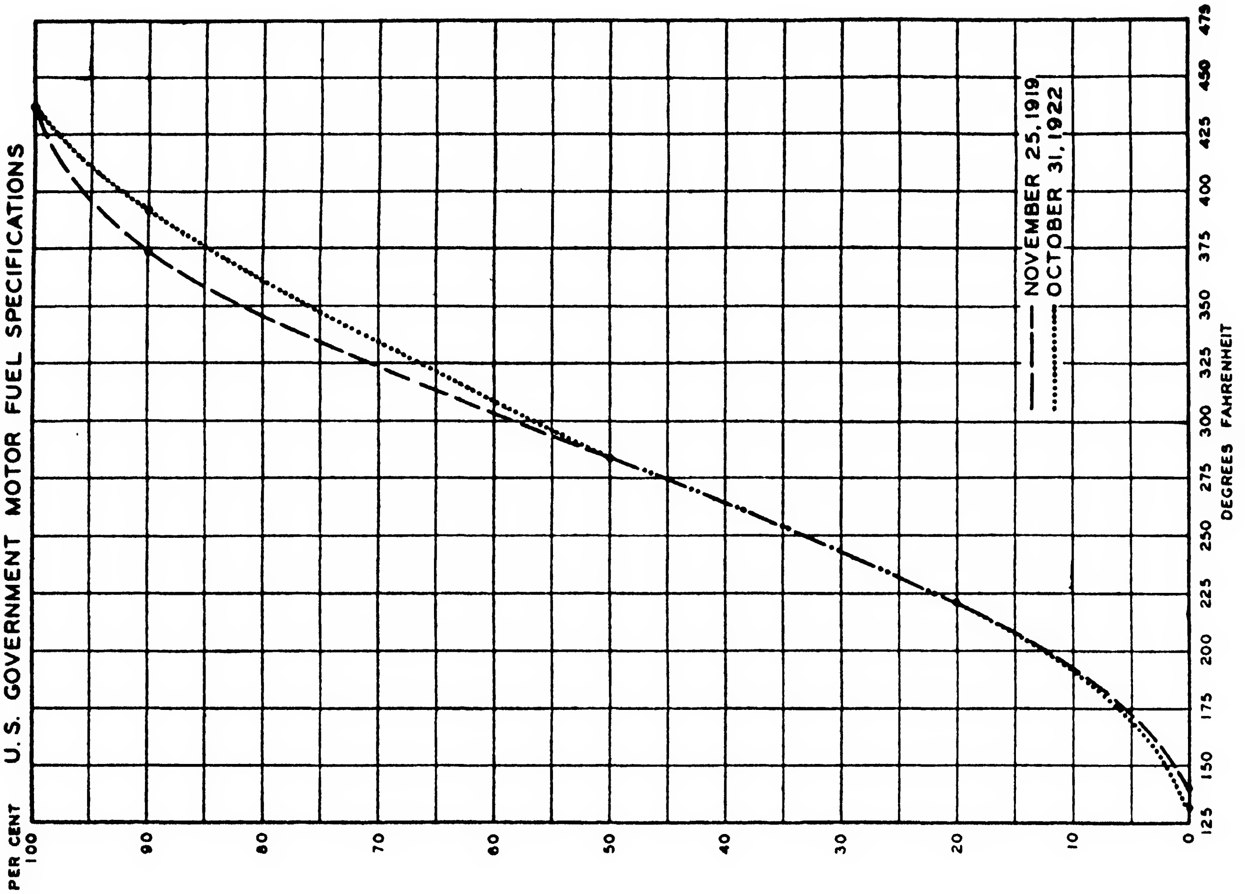

U. S. GOVERNMENT MOTOR FUEL SPECIFICATIONS
PER CENT
100
90
80
70
60
50
40
30
20
10
0
125
150
175
200
225
250
275
300
325
350
375
400
425
450
475
DEGREES FAHRENHEIT
NOVEMBER 25, 1919
OCTOBER 31, 1922

FIG. 5.

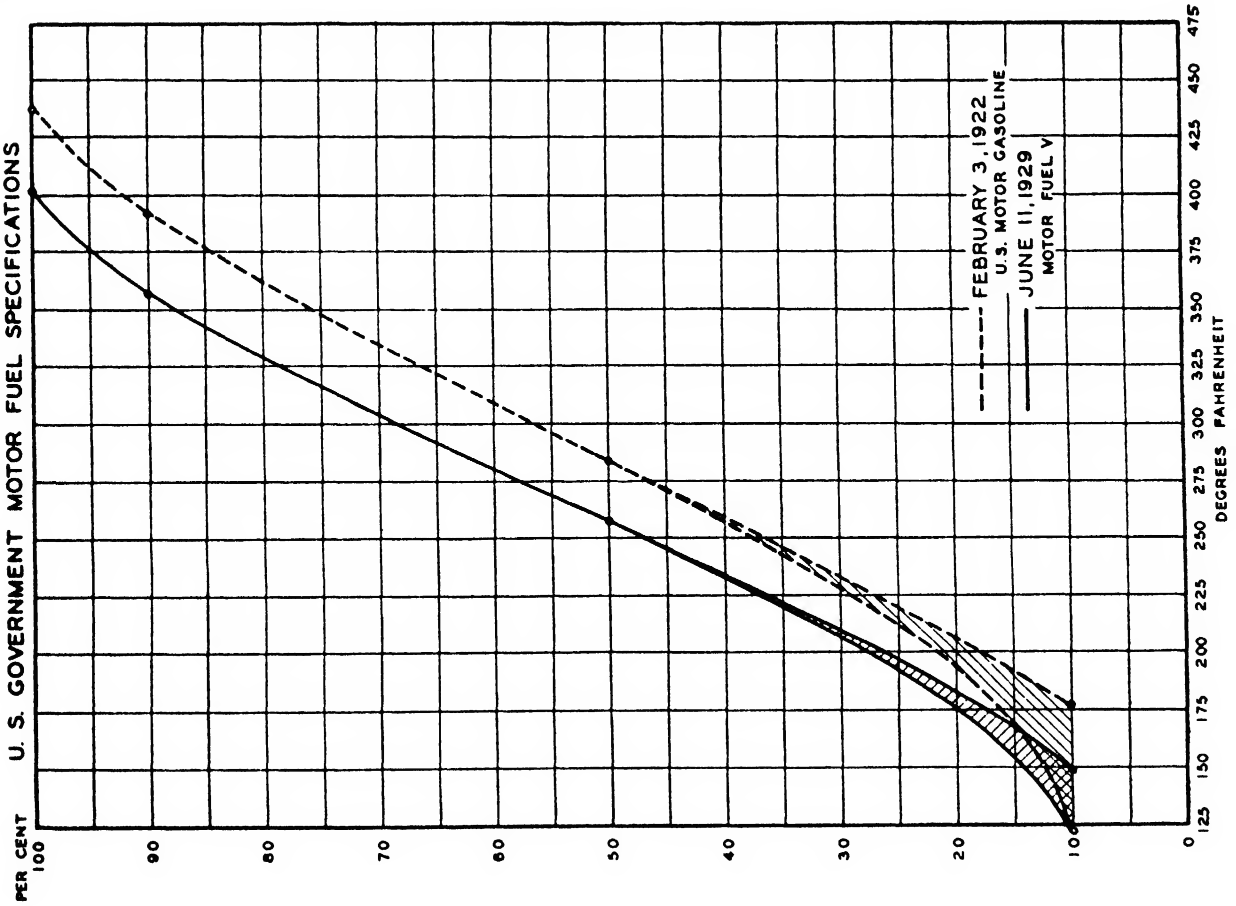

U. S. GOVERNMENT MOTOR FUEL SPECIFICATIONS
PER CENT
100
90
80
70
60
50
40
30
20
10
0
125
150
175
200
225
250
275
300
325
350
375
400
425
450
475
DEGREES FAHRENHEIT
FEBRUARY 3, 1922
U.S. MOTOR GASOLINE
JUNE 11, 1929
MOTOR FUEL V

Fig. 6.

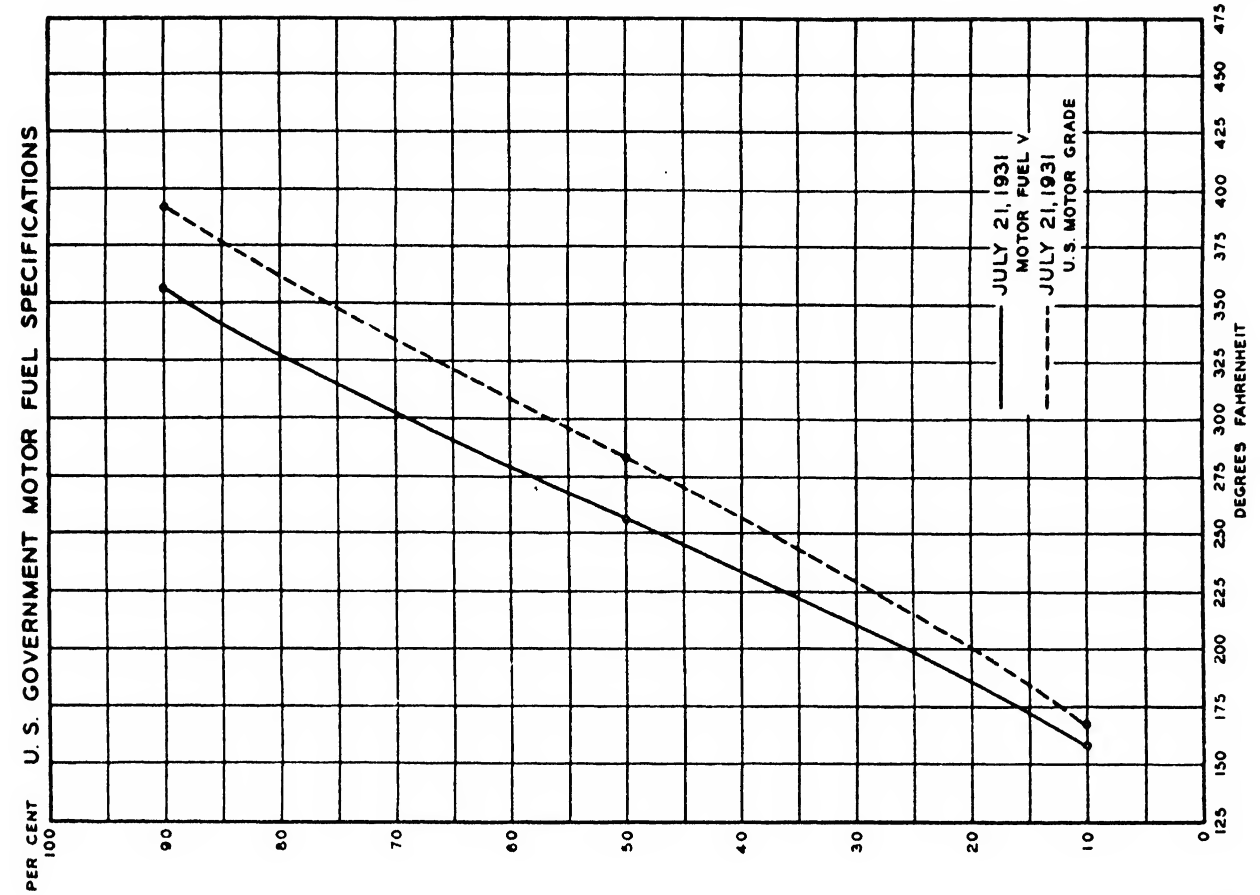

U. S. GOVERNMENT MOTOR FUEL SPECIFICATIONS
PER CENT
100
90
80
70
60
50
40
30
20
10
0
125
150
175
200
225
250
275
300
325
350
375
400
425
450
475
DEGREES FAHRENHEIT
JULY 21, 1931
MOTOR FUEL V
JULY 21, 1931
U.S. MOTOR GRADE

Fig. 7.

It will be evident to any one studying the question of gasoline specifications that the changes have resulted from changes in the design of fuel systems of cars, making necessary the elimination of certain of the points formerly considered of importance which are now known to be of minor value; these will be discussed further under the subject of properties. For instance, the elimination of the gravity and the initial boiling-point and end-point, also other changes or limits in the 10%, 50%, and 90% distillation readings which will govern the volatility of the product; the control of the vapour pressure and the anti-knock properties.

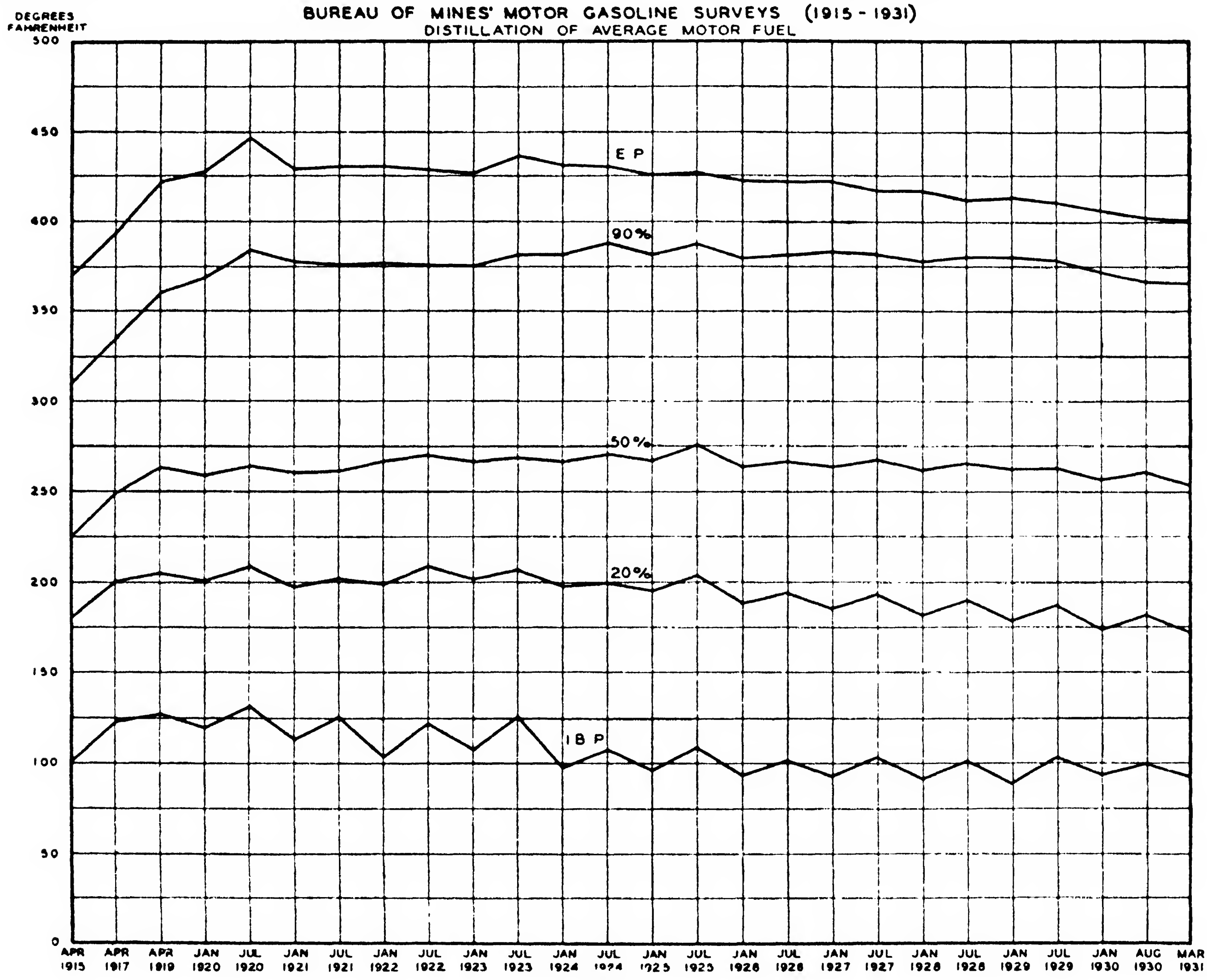


Fig. 8.

The Government specifications for gasoline are in many cases also adopted by the different States, although the States use these specifications principally for taxation purposes. There are a number of States which do not have any specifications at all, and there are States where variations from the Government standard are made and for taxing purposes certain arbitrary classifications are used which do not agree with the actual specifications. For instance, in the State of Oklahoma, kerosine is defined as a product having among other properties a gravity range of 40 to 48° Bé., both inclusive, and also a certain flash requirement. On the other hand, in the tax law they classify as gasoline any petroleum product having a gravity lighter than 44° Bé. Anomalies of this sort exist in other State requirements as well, but an extra volume would be required to cover all the different State tax law requirements because of the rapidly changing situation due to efforts towards finding new sources of revenue.

Fig. 8 shows the changes in volatility of the gasoline marketed in the years 1915 to 1931 on the basis of surveys made by the U.S. Bureau of Mines [23]. It will be seen in comparing the last survey's figures with the average of tests from a nation-wide survey made in 1934, that the average gasoline is much more volatile than it was in the years just after the World War, 1919 to 1920. The development of the cracking processes which became of importance during the War and shortly thereafter greatly augmented the supply of gasoline and also improved the quality from an anti-knock standpoint. As indicated in Fig. 3, the amount of cracked gasoline produced in 1934 was almost equal in amount to the straight-run product.

Improvements in distillation and refining methods, combined with an abundance of crude, have enabled the oil companies to provide the motoring public with a nearly perfect motor fuel. This is indeed fortunate, since even the low-priced cars have been brought to such a state of mechanical perfection that satisfactory performance is taken as a matter of course. The technical branch of the petroleum industry has, for the past several years, been devoting a major portion of its activity towards the solution of the problem, 'What constitutes a Satisfactory Motor Fuel?' These scientific investigations have resulted in improved products, as reflected by the trend shown in the surveys and specifications previously described.

The fundamentals underlying this fuel problem are now pretty definitely known. Laboratory tests have been developed that enable one to predict a fuel's service performance with a reasonable degree of accuracy. The following is an attempt to summarize the enormous amount of research work that has been reported on this subject.

Properties of a Satisfactory Motor Fuel

A satisfactory motor fuel should meet the following requirements:

1. Volatility should be such that the engine will start easily, warm up quickly, accelerate satisfactorily, operate without crankcase oil dilution, and be free from vapour lock.
2. The anti-knock rating should be sufficiently high so that the fuel can be used in the modern high-compression engine without detonation.
3. It should be free from gum-forming compounds that would result in engine deposits.
4. It should be free from abrasive or corrosive substances which might result in injury to the engine.

Volatility.

The question of volatility has been the subject of a great deal of research. Among the important investigations are the following:

1. A study of fuel volatility and its relationship to service requirements conducted by the Co-operative Fuel Research Committee, a joint group formed by the automotive and petroleum industries. The National Automobile Chamber of Commerce and the American Petroleum Institute sponsored the investigation. The research work was conducted by the Bureau of Standards. The work extended from 1922 to 1930, progress reports being published in various issues of the *S.A.E. Journal* during that period. This investigation has been summarized by Dickinson [6, 1929–30].
2. An investigation of vapour lock by the Bureau of Standards, sponsored by the Natural Gasoline Association and directed by the Cooperative Fuel Research Committee. This work was carried out from 1930 to 1932 and was reported at various times in the *S.A.E. Journal.*

In addition to these there have been many private investigations. Oberfell [17, 1935] has published a very excellent bibliography on the subject of volatility.

Correlation of Laboratory Tests with Actual Performance

In general, for American cars of current production, it can be stated that actual performance correlates with the A.S.T.M. Distillation Test on Gasoline (D. 86–30) as follows:

'Initial boiling-point' has no significance.

The 10% point governs ease of starting and with the vapour pressure determines a fuel's vapour-locking characteristics.

The 50% point controls the warming-up period.

The 90% point indicates the dew-point which determines the proper manifold temperature; thus it has some influence on power, economy, and acceleration. The 90% point also establishes limits for prevention of crankcase oil dilution.

The end-point has no significance.

Starting.

If starting occurs with 10 revolutions of a cold engine in winter weather, the driving public considers the starting performance satisfactory. Various investigators agree that the ease of starting correlates well with the A.S.T.M. 10% evaporated point. The relationship between the 10% point and the atmospheric temperature at which satisfactory starting will occur is shown by Dickinson [6, 1929–30] and Brown [2, 1930]. Since these two investigations agree within an atmospheric temperature of 10° F., only the average is shown:

Atmospheric temperature	*Maximum A.S.T.M. 10% evaporated point for satisfactory starting*
−20° F.	97° F.
0 ,,	127 ,,
+20 ,,	160 ,,
+40 ,,	190 ,,

The average American winter gasoline has a 10% evaporated point of 127° F. and should, therefore, provide satisfactory starting down to 0° F. Below that temperature starting would be possible, but more difficult.

As the atmospheric temperature decreases, the viscosity of the lubricating oil, the condition and size of battery, and other factors assume increasing importance.

Vapour Lock.

To meet the exacting performance demands of the motoring public the gasoline refiner must produce a product that will not vapour lock in a great majority of cars even under severe conditions. If a gasoline is overheated during its passage through the fuel system, gasification of the fuel causes the formation of bubbles, which influence the amount reaching the engine. As a result vapour lock, faltering, or stalling of the engine may occur.

Investigators agree that the vapour-locking tendency of a gasoline is a function of the A.S.T.M. 10% evaporated point and the Reid vapour pressure. In the majority of commercial gasolines now being marketed the Reid vapour pressure is, however, the controlling factor. There is considerable disagreement among investigators as to the exact correlation between the vapour pressure as determined in the laboratory and the vapour-locking tendency in service. This is to be expected due to the numerous experimental difficulties involved in the study of vapour lock. The following relationship represents the average findings of several thorough research programmes:

Atmospheric temperature	*Maximum Reid vapour pressure to prevent vapour lock*
50° F.	14 lb.
60 ,,	12 ,,
70 ,,	11 ,,
80 ,,	9·5 ,,
90 ,,	8 ,,
100 ,,	7 ,,

This problem is still being studied by the A.S.T.M., and the above relationship must be considered approximate and subject to change with automotive design. The average American summer gasoline has a Reid vapour pressure of 7 lb. and could, according to this table, be considered satisfactory.

Much can be done by the motor manufacturer to cool further the fuel system, thus permitting the use of a more volatile fuel with resultant improvement in ease of starting, anti-knock, and manifold temperature.

MacCoull [14, 1935] suggests the following methods for preventing vapour lock:

A. Place the carburettor away from the exhaust pipe, if possible.

B. Encourage large air-volume passage through the radiator while the car is running, and circulation by convection when the engine is idling. This requires ample louvers placed high enough to let air out over the engine and free passage out at the bottom.

C. Shield carburettor and fuel pump from exhaust radiation and convection.

D. Insulate carburettor flange from manifold and fuel pump from crankcase.

E. Reduce mass of exhaust pipe.

F. Apply sufficient heat between fuel pump and carburettor intake to boil off in the carburettor bowl that part of the fuel which would otherwise boil in the carburettor jet and cause vapour lock. The minimum possible volume of liquid should be thus heated, and an ample vent must be provided at the carburettor bowl to carry off the vapour formed.

G. Carburettor jet should be raised an appreciable distance above normal level of the float chamber, and a large liquid area is desirable to prevent flooding as the gasoline boils.

Since, under certain conditions, from 5 to 10% of the gasoline that flows through the fuel system is boiled off at the carburettor, there is a direct loss in fuel economy when vapour lock is prevented by venting the carburettor instead of by the preferred method of reducing fuel-line temperature.

According to Boyd [4, 1935], the average maximum temperature rise in the fuel system of representative cars is as follows:

1929 .	. 73° F.
1931 .	. 66 ,,
1934 .	. 57 ,,

Dickinson [6, 1929–30] and MacCoull [14, 1935] state that the boiling-point of a gasoline in the fuel system is approximately equal to the A.S.T.M. 10% distillation point. The average American summer gasoline, which has a 10% point of 149° F., will therefore boil in the average car at atmospheric temperatures above 90° F. Although this would indicate that the average gasoline is satisfactory in the average car, a reduction in fuel-line temperatures is necessary to permit the economical use of a more volatile gasoline.

Warming Up.

After the engine is started, it is desirable that the choke be used as little as possible, not only for the driver's convenience, but also to prevent dilution of the lubricating oil. Various authors have stated that the lower the A.S.T.M. 50% point, the less choke will be required.

According to Boyd [4, 1935], in 1935 over half of the American cars were equipped with automatic chokes, the purpose of which is to provide the correct fuel to air ratio for every starting and running condition. It is particularly important that the automatic choke work properly during the warming-up period. According to Jorgensen [12, 1935], the setting of the automatic choke is dependent on the volatility of the gasoline being used, the 50% point being the controlling factor. He states that in the summer there is approximately 100° F. temperature difference between the 50% points of different brands of gasolines, and that to take care of this range three different automatic choke settings are necessary. He stresses the need of greater uniformity of the 50% points of the gasolines now on the market to reduce the necessity of readjustment of the automatic choke.

Acceleration.

According to Barnard [1*a*, 1934], improvement in volatility of a gasoline, either at the beginning or end of the distillation curve, will result in better acceleration. This is not in contradiction to his previous contention [25, 1930] that the 50% point correlates best with acceleration characteristics. Brown [3, 1935] supports this contention. Brown [2, 1930] established the relationship between atmospheric temperature and minimum 90% point required for good acceleration. MacCoull [13, 1933] found that a fuel with a 90% point of 300° F. gave a maximum acceleration at 70° F. atmospheric temperature. However, there was little difference between fuels having 90% points between 250 and 400° F.

Crankcase Oil Dilution.

Commercial gasolines appear satisfactory from the standpoint of preventing crankcase oil dilution and, as a result, there are little recent data on the correlation of this property with the A.S.T.M. distillation of gasoline. There is little doubt but that the 90% point is the controlling factor. The universal adoption of crankcase ventilating systems is largely responsible for present freedom from dilution. The work at the Bureau of Standards led to the following conclusions:

1. Dilution decreases with:
    A. An increase in engine-cylinder wall temperature;
    B. An increase in air-fuel ratio; and
    C. An increase in crankcase temperature.
2. Dilution is not much affected by air temperature, piston and piston-ring fit, or oil viscosity.
3. Dilution of crankcase oil is consistently greater the less volatile the fuel, the 90% point on the A.S.T.M. distillation curve being taken as an index of volatility.
4. Dilution of crankcase oil is much greater in cold weather than in warm weather.

Economy.

According to Ricardo [19, 1927], apart from the limitations introduced by detonation, the efficiency with which all gasolines are burned is practically the same at the same compression ratio, and with the same amount of heat added at the manifold, since the energy liberated per cubic inch of a combustible mixture is practically constant for most fuels. There is some evidence, however (MacCoull [13, 1933]), which indicates that the modern car produces maximum economy when operating with gasolines having 90% points ranging from 340 to 400° F., the drop in miles per gallon of the lighter fuel being due to a lower volumetric heating value, while the decreased economy of the less volatile gasoline may be ascribed to imperfect distribution.

The Bureau of Standards tests showed that gasoline consumption in miles per gallon is somewhat greater in winter than in summer.

The present trend towards heavier cars and higher speeds is tending to decrease economy in terms of miles per gallon. However, this is being offset by continual improvements in engine design and by the use of higher compression ratios and lower mixture temperatures made possible by improvements in gasoline anti-knock rating and volatility.

Improved performance obtained by using a more volatile fuel may be offset by loss by evaporation in the fuel system, which may exceed 5 or 10%, depending on the fuel system temperatures.

Power.

Although, as pointed out by Ricardo, there is no doubt but that the potential difference in power between various gasolines is small, tests by MacCoull [13, 1933] indicate that present-day cars produce maximum power with gasolines having A.S.T.M. 90% points between 300 and 360° F.

Power can be increased considerably, however, by using a more volatile gasoline if the engine is designed for the more volatile fuel, so as to have the least manifold heat consistent with proper distribution, since at the lower manifold temperatures a denser and more powerful charge enters the engine.

Barnard [1*a*, 1934] calls attention to the fact that, because of the lesser tendency to detonate with the colder mixtures, if reductions can be effected in mixture temperatures by using a more volatile fuel, an increase in compression ratio may be permitted for any given octane number of motor gasoline. The effect of mixture temperature is in the order of 0·25 compression ratio for each 30° change. He estimates that, if advantage were taken of the two effects—improved volumetric efficiency and higher compression ratio—the brake horse-power might be increased 10% for a 30° decrease in the mixture temperature.

According to MacCoull [13, 1933], the dew-point of a gasoline may be predicted from the A.S.T.M. 90% point, as follows:

A.S.T.M. 90% point	*Dew-point 12:1 air/fuel ratio*
240° F.	43° F.
280 ,,	70 ,,
320 ,,	100 ,,
360 ,,	128 ,,
400 ,,	157 ,,

The average American gasoline, which has a 90% point of 354° F., accordingly has a dew-point of 124° F. To ensure perfect distribution American cars should, therefore, have a manifold temperature above 124° F.

Boyd [4, 1935] reports that representative mixture temperatures have been as follows:

1931	117° F.
1932	110 ,,
1933	103 ,,
1934	90 ,,

This would indicate that manifold temperatures are below the dew-point of the average gasoline and, therefore, insufficient to provide perfect distribution. This point cannot be definitely determined, however, since Boyd has stated that his figures on mixture temperatures are presented with full realization of the shortcomings of mixture temperature measurements as ordinarily made. Nevertheless, sacrifice is apparently being made from the standpoint of perfect distribution to gain the improvement in power that results from using lower mixture temperatures.

Anti-knock.

The problem of detonation first arose in the United States with the introduction of engines of higher compression ratio (which is the ratio of the volume above the piston at the lowest point of its travel to the volume above it at the highest point in its travel). The theory of the mechanism of detonation is still by no means clear, although many investigations of undoubtedly excellent character have been made. The knock may be avoided, but with a consequent loss in power and efficiency, by such means as retarding ignition timing, enriching the fuel mixture, or lowering the engine compression ratio.

In 1928 the Co-operative Fuel Research Committee, a joint committee from the automotive and petroleum industries, together with a similar group in England, known as Committee D. 9 of the Institution of Petroleum Technologists, undertook the development of a laboratory test to measure the anti-knock property of fuels.

Since there appeared to be no correlation between anti-knock quality and ordinary chemical tests, the only alternative was the development of a laboratory engine in which the anti-knock value of a fuel is measured by matching its knocking tendency against reference fuels of arbitrarily assumed anti-knock value. A single-cylinder laboratory engine was developed through a large amount of research work and is now being manufactured by the Waukesha Motor Company. The primary reference fuels adopted—*iso*-octane and normal heptane—were originally recommended by Dr. Graham Edgar. Secondary reference fuels, made generally available by the Standard Oil Development Company, are used in routine testing.

Early experimental work showed that the octane number, or relative anti-knock value, of different fuels depended on the conditions under which the test engine operated. To determine what laboratory procedure would best correlate actual road performance, extensive road tests were conducted in 1932 at Uniontown, Pa. As a result of these road tests, in which the knock rating of typical fuels was determined in representative American cars, a reasonably accurate laboratory procedure has been worked out and has been adopted as a tentative standard by the A.S.T.M., known as D. 357–33T, Knock Determination of Motor Fuels.

The very rapid increase in the compression ratio of American passenger-car engines during the last 10 years is shown by Fig. 9. This covers only standard models and not the special high-compression heads available for some cars; in 1934, for example, while only one standard model had a compression ratio above 7:1, optional heads were available in nine cars, ranging from 7:1 to as high as 7·45:1. This increasing compression ratio has resulted in a demand for higher and higher anti-knock fuel which has been met by the increasing use of cracked gasoline, 're-forming' of straight-run gasoline, and the use of tetraethyl lead. While only about 3·5% of the total gasoline used in 1934 was 'leaded' to the premium fuel standard, 76 octane, yet over 60% contained smaller quantities of ethyl fluid to bring the gasoline up to 70 octane (maximum), the so-called 'Q' standard. The balance, about 35%, represents consumption of unleaded regular gasoline and third-grade gasoline.

The octane ratings of the gasolines of all the major distributors fall in general in one of the three classifications for anti-knock; the premium grade of 76 octane rating either ethyl or its equivalent, the regular grade of 70 octane, known also as 'Q' gasoline when the anti-knock rating is obtained by the addition of ethyl fluid, or by cracking; third grade which varies in octane rating from 50 to 60.

Tests of the 1934 model cars indicate anti-knock requirements ranging between 65–75 octane units if knock-free performance is desired.

Many of the causes for this variation in anti-knock requirement are reported by Hawley and Bartholomew [10, 1934], who show that the fuel octane required to prevent knock:

1. Decreases with improved valve and piston cooling.

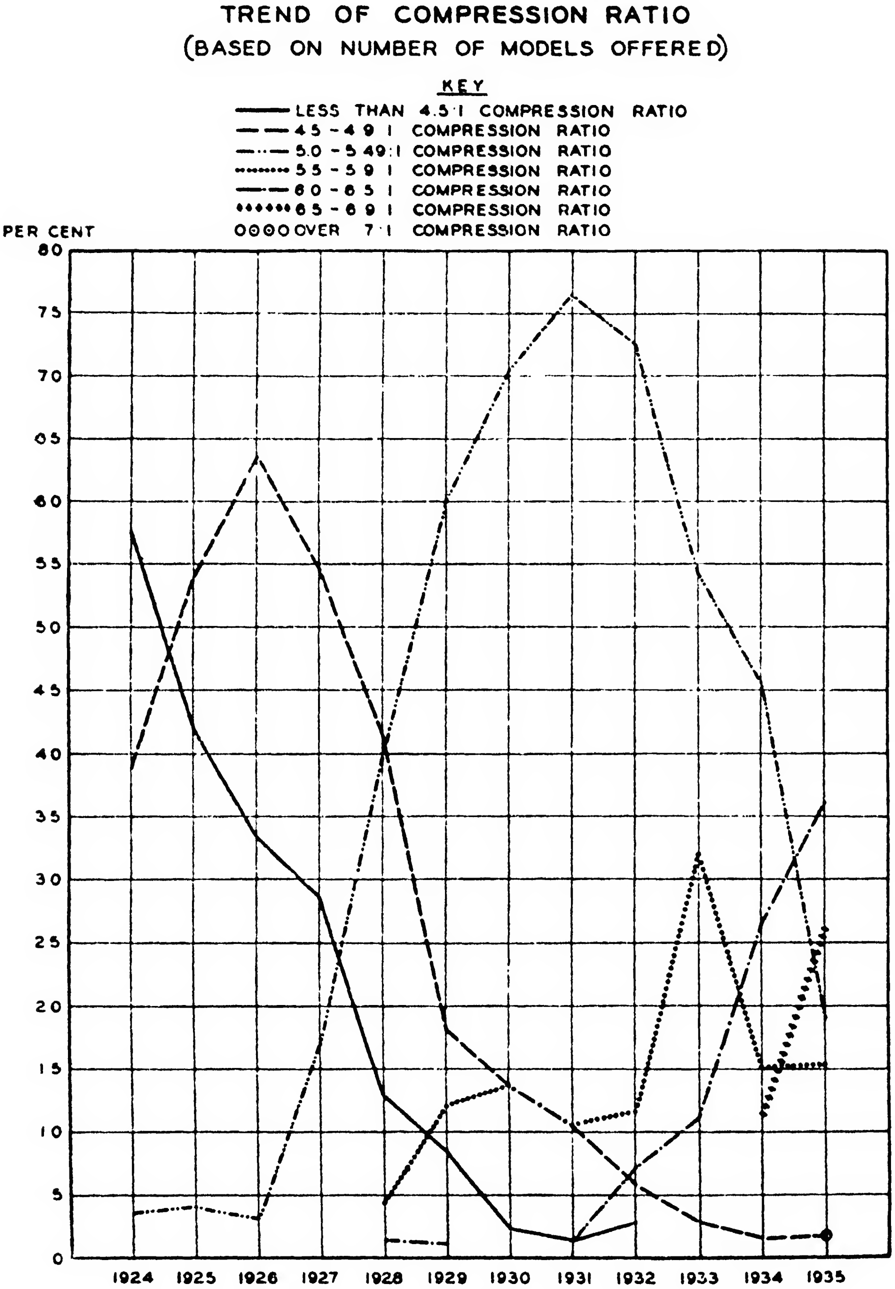


Fig. 9.

2. Decreases as the cylinder diameter is reduced.
3. Is lower with aluminium than cast-iron cylinder heads.
4. Increases with accumulation of carbon in combustion chamber.
5. Varies with engine speed; the speed for maximum knock depending on the individual characteristics of the engine.
6. Decreases with a reduction in jacket temperature.
7. Varies with mixture ratio; the air/fuel ratio for maximum knock being not far different from that for maximum power.
8. Decreases as intake temperature is reduced.
9. Decreases as the volumetric efficiency is reduced by closing the throttle.
10. Decreases as the spark timing is retarded.
11. Decreases as the compression ratio is lowered.

While the 're-forming' or molecular rearrangement by heating under pressure of knocking gasolines has been in commercial refinery operation for a number of years, it is only recently that claims of successful isomerization of pure paraffin hydrocarbons have been advanced. Nenitzescu and Dragan [16, 1933] by means of aluminium chloride catalyst at 68° C. obtained from *n*-hexane a mixture of 2- and 3-methyl pentane. Petrow [18, 1935] also obtained *iso*-paraffins from heptane and octane by heating to 400–500° C. in presence of various catalysts. This is an important development, for while such normal paraffins have very low anti-knock ratings, that of some of their isomers is well above 100. There is thus the possibility of separating a crude fraction corresponding to the hexane-octane range and re-forming it under isomerizing conditions of temperature, catalyst, &c.

What promises to be a more definite development, however, in the synthesis of higher octane motor fuel is the polymerization of unsaturated cracking gases by means of phosphoric acid and other catalysts, as well as the heat treatment of the gaseous paraffins. Since these processes were described in detail during the Symposium on the Chemistry of Gaseous Hydrocarbons at the 1934 spring meeting of the American Chemical Society, they will not be discussed in this article.

Supplemental Tests

As previously stated, the operation of the engine is concerned only with the volatility and the anti-knock rating of the fuel. From a stability standpoint the question of gum, sulphur, and to some degree colour and odour, may be given some attention, although only the question of gum and sulphur at the present time is considered of any great importance.

Gasoline, particularly that formed from cracking under vapour-phase conditions, if stored for any considerable period, tends to deposit a resinous material and may form similar gummy deposits in the gasoline tank and around the intake valve of an engine. This tendency of a gasoline to form gum may result in stoppage of the lines to, or the passages in, the carburettor, but it has not been definitely shown that gum formation, unless very large in amount, is a serious objection.

It has been shown by the work of Voorhees and Eisinger [24, 1929] that it is only the 'preformed' or actual gum in gasoline that causes trouble in the engine. The copper dish test, which involves evaporating 100 c.c. of gasoline in a polished copper dish in the steam bath, drying to constant weight, and weighing the residue, was for years the only recognized test for gum. It is very generally recognized that this method of test is difficult to check, but is considered of value in predicting the behaviour of the gasoline in storage, since it is a rough measure of the potential or gum-forming proclivities of a gasoline.

The actual gum has been determined in the past by the evaporation in the steam oven, such as the method of Cooke [5, 1925].

A recent study of these various test methods indicated that none are wholly satisfactory in predicting gum formation in practice, nor has the amount of formed gum which the engine will tolerate been definitely established. The A.S.T.M. tentative method of test for gum content of gasoline involves rapid evaporation of a sample of gasoline (A.S.T.M. D. 381–34T) at elevated temperature in a current of heated air. Since the amount of gum obtained from an aged gasoline depends upon the conditions of evaporation, the numerical results obtained by this method will not be the same as obtained by other evaporation methods, but the results obtained by these methods should parallel one another.

The A.S.T.M. has not yet standardized a method for determination of gum stability. Methods which are in use to give this indication are the bomb test of the Ethyl Gasoline Corporation [9, 1930] and the U.S. Army bomb test [22, 1935]. In these tests the induction time is measured as well as the actual gum formed during the test. The method of Voorhees and Eisinger [24, 1929] is also used for this purpose, and it is claimed by Rogers [20, 1933] that an induction period of 400 minutes corresponds to approximately a year of storage life in vented iron barrels.

Considerable benefit from the standpoint of stability results from the use of small amounts of various organic substances for inhibiting oxidation, which has been rather definitely established as the primary cause of gum formation in gasoline. It is desirable, however, that antioxidants of the highest effectiveness should be used so that the amount required is not sufficient to alter adversely any other property of the gasoline. Quite a wide variety of materials are used for this purpose. Amino-phenols are among the most effective, but they are in general too insoluble in gasoline for practical use. Introduction of benzyl groups into para-amino-phenol renders the amino-phenol much more soluble in gasoline than in water. According to Rogers and Voorhees [21, 1933], butyl and amyl amines have been found to exert a protective or stabilizing action on inhibitors, thus making it possible to use in 'water-white gasoline'.

It has also been found that compounds already present in the crude fuel are capable of acting as inhibitors; there are also compounds present which accelerate gum formation. Both of these classes of material should be removed as far as possible before the addition of inhibitors, or the inhibitor added will produce little effect or may even increase gum [11, 1933].

Inhibitors of value from both the standpoint of gum and colour have been found, but in most cases some treatment is necessary to ensure freedom from this trouble. It is not possible, except with very few cracked fuels, to depend entirely on inhibitors without some treatment for improving naphtha to ensure stability of the finished product. It is the practice of most large refiners to conduct storage tests over a long period of time, at least 6 months to 2 years, in connexion with any new process of refining or stabilization by inhibitors before one can be definitely assured that the proposed treatment will give a product of satisfactory stability under varying storage conditions.

Colour.

With the introduction of ethyl gasoline which, by order of the Surgeon-General of the United States Army, must be coloured red of a certain definite intensity, the question of colour or of refining to a so-called water-white colour became of little significance. This was recognized by the U.S. Government eliminating colour tests from its specification. The fact that cracked gasolines tend to be much yellower in colour and to have more gum than ordinary gasoline led many to believe that colour was an indication of gum or gum-forming constituents, but it has been shown repeatedly that yellow gasolines may contain practically no gum, and water-white gasolines may contain large quantities of potential gum. Therefore colour cannot be relied upon as an indication of freedom from gum, and it is now the practice of many refiners to colour gasolines of a particular brand a distinctive colour. We therefore have gasolines of all the colours of the rainbow. With the introduction of 'Q' gasoline which contains a certain amount of lead, the colouring of this product was also mandatory and is ordinarily a copper or orange shade.

Odour.

In the early marketing of gasoline the question of odour was of great importance. This property is most difficult to define and as yet there exists no definite method of measurement, but it was the custom among refiners to use such terms as 'sweet', 'sour', or 'cracked' and 'aromatic' to indicate the odours of different gasolines. The ancient 'doctor test' was and is still used, particularly in connexion with straight-run products, to indicate presence of or freedom from sulphurous products. It affords a simple means of detecting the presence of mercaptans or dissolved hydrogen sulphide in gasoline, but it seems to overlook one of the most corrosive substances, 'dissolved sulphur'. With the wider use of cracked gasolines the question of odour has largely disappeared, and no specifications for motor fuels now contain any reference to this rather elusive property.

Sulphur.

The corrosion of fuel lines due to free sulphur or sulphur compounds in the gasoline is not often encountered, but almost all gasolines are marketed to meet the copper-strip corrosion test, A.S.T.M. D. 130–30. However, crankcase corrosion does sometimes occur due to formation of sulphur dioxide by combustion of sulphur in the fuel. Some of the combustion gases of sulphur leak past the piston-rings and combine with moisture in the crankcase to form corrosive acids. While crankcase ventilators reduce the amount of water present in the crankcase, there is still considerable difference of opinion as to possible danger from this type of corrosion. As a factor of safety the Government specifications still retain the 0·10% maximum total sulphur content.

There has recently been proposed an elaborate series of tests by the Ethyl Gasoline Corporation which are to be run in California [1, 1935]. Among other investigations covered in this series of fuel tests they intend to determine the effect of dyes and concentration of sulphur compounds on fuel behaviour in engines.

In general the gasoline surveys made in the United States [23] indicate that in practically all parts of the country, with the possible exception of California, the sulphur content of gasolines sold comes under the maximum 0·10% (specified by the Government). In California gasolines are sold with as high as 0·25% sulphur, and there has been no evidence that this higher content has caused any trouble in use. There have been two papers published by Diggs [7, 1928] and Mougey [15, 1928] which showed very rapid and serious corrosion of wrist pins, bearings, starter chains, and even cylinder walls from a gasoline containing a higher content of sulphur than 0·1%, under conditions of winter driving and in cars fitted with unventilated crankcases.

Gravity.

Gravity, which was formerly the only specification for gasoline and is still retained in some State specifications, is now considered by practically every one having to do with gasoline specifications of no significance from a practical standpoint. It is generally relatively true that a lighter gravity gasoline indicates a poorer product from the standpoints of knocking and fuel economy than a heavier gravity gasoline.

Addition of Lubricating Oil to Gasoline.

Some gasolines are marketed containing a small quantity of lubricating oil. It is alleged that this addition is desirable from the standpoint of upper cylinder lubrication. From the evidence available on this question, it is the opinion of the writer that the addition of lubricating oil in the amount found seems to do no harm.

Special Motor Fuels

Benzol Blends.

The quantity of benzol available for motor-fuel blending purposes is so limited in the United States that little consideration need be given to its use here. Certain motor fuels containing 20 to 40% of benzol are being marketed where a local supply of benzol is available. Such blends are satisfactory both from the standpoint and from the standpoint of detonating tendencies.

REFERENCES

1. Barth, E. *Oil and Gas J.*, 28 March 1935, 66.
1*a*. Barnard, D. P. *J.S.A.E.* **34**, 26–7 (1934); **35**, 399–401 (1934).
2. Brown, G. G. Univ. of Michigan Eng. Res. Bull. no. 14 (1930).
3. —— *Nat. Petr. News*, 8 May 1935, 24A.
4. Campbell, J. M., Lovell, W. G., and Boyd, T. A. *Trends in Engine Design as Influenced by Fuel Volatility.* (Preprint 1935 Summer Meeting, S.A.E.)
5. Cooke, M. B. U.S. Bureau of Mines, Serial no. 2686 (1925).
6. Dickinson, H. C. *J.S.A.E.* **25**, 171–4 (1929); *Trans. 2nd World Power Conf.* (Berlin), **8**, 3–20 (1930).
7. Diggs, S. H. *Ind. Eng. Chem.* **20**, 16 (1928).
8. Eisinger, J. O., and Barnard, D. P. *Oil and Gas J.*, 11 July 1935, 34, 37, 39–40.
9. Ethyl Gasoline Corporation. Rept. no. 18, 20 June 1930.
10. Hawley, C. D., and Bartholomew, E. *Nat. Petr. News*, 23 May 1934, 20F–20J.
11. Hoffert, W. H., and Claxton, G. *Proc. World Petr. Cong.*, **2**, 69–76 (1933).
12. Jorgensen, C. H. *What Price Dynamite?* (Preprint 1935 Summer Meeting, S.A.E.)
13. MacCoull, N. *J.S.A.E.* **33**, 363–70 (1933).
14. MacCoull, N., and Barber, E. M. *J.S.A.E.*, July 1935, 237–46.
15. Mougey, H. C. *Ind. Eng. Chem.* **20**, 18 (1928).
16. Nenitzescu, C. D., and Dragan, A. *Ber.* 1892 (1933).
17. Oberfell, G. G., Alden, R. C., and Trimble, H. M. *Oil and Gas J.*, 4 July 1935, 45-9.
18. Petrow, A. D., *Ber.* 1–5 (1935).
19. Ricardo, H. R. *High Speed Engines* (1927).
20. Rogers, T. H. *Ind. Eng. Chem.* **25**, 397–403 (1933).
21. Rogers, T. H., and Voorhees, V. *Proc. World Petr. Cong.*, **2**, 63–8 (1933).
22. U.S. Army, Air Corps, Specn. no. Y-3557-H (15 April 1935).
23. U.S. Bureau of Mines. T.P. 163; Bull. 191; R.I. 2083, 2220, 2272, 2328, 2388, 2525, 2577, 2636, 2675, 2703, 2740, 2765, 2795, 2827, 2861, 2887, 2916, 2959, 2995, 3063, 3092, 3129, 3142, 3152, 3162, 3175.
24. Voorhees, V., and Eisinger, J. O. *J.S.A.E.* **24**, 284 (1929); *Proc. A.P.I.* **10**, no. 2, 169 (1929).
25. Wilson, R. E. *A.S.T.M. Symposium on Developments in Automotive Materials*, 103–26 (Detroit, 19 March 1930).

SELECTED BIBLIOGRAPHY

American Petroleum Institute, Statistical Bulletins.
A.S.T.M., Committee D. 2. The Significance of Tests of Petroleum Products (1934).
Ellis and Meigs. *Gasoline and Other Motor Fuels* (1921).
Gruse. *Petroleum and Its Products* (1928).
Leslie. *Motor Fuels* (1923).
Nash-Howes. *The Principles of Motor Fuel Preparation and Application*, **1** (1934).
Wilson, R. E. Significance of Tests for Motor Fuels, *Oil and Gas Journ.* 17 July 1930, 40; 24 July 1930, 38.
World Petroleum Congress, London, 1933. *Proc.* **2**.

MOTOR FUELS IN EUROPEAN COUNTRIES

By F. H. GARNER, Ph.D., F.I.C., and E. W. HARDIMAN, B.Sc.
Anglo-American Oil Co., London, England

SPECIFICATIONS for motor fuels marketed in various countries vary according to climatic conditions and the compression ratios of the engines in both passenger and commercial vehicles, but in certain European countries the use of such blending agents as alcohol and benzol has led to a greater variation in the tests of these fuels than is found in other countries, more particularly than in the United States.

The use of alcohol as a blending agent in gasolines is discussed from the point of view of performance in the article by Howes on Special Engine Fuels, p. 2444, but the most important factor underlying this use of alcohol is not that of performance, but rather that of national economics. In no country can alcohol be produced at a price which is comparable with that of duty-free gasoline from crude petroleum, and thus the main factor in the extended use of alcohol in Europe is political, and is due to the trend towards economic nationalism and self-sufficiency. A similar factor has operated towards increasing the recovery and supplies of benzol available, but benzol production is primarily dependent on either steel or gas manufacture, and is thus a normal by-product, whereas alcohol is primarily produced either from food material or from imported materials such as molasses, and only in rare instances is it a by-product, as, for example, in Sweden, where the alcohol is recovered from by-products of the paper industry.

Past experience has shown that both alcohol and benzol are diverted from motor fuels to other uses in times of national emergency, leading to considerable difficulties in meeting specification requirements, more particularly as regards octane numbers, which have been based on the admixture of these two fuels.

Most of the experimental work on fuels carried out in Europe has been on knock tendency, and practically all the information on the relation between ease of starting, warming-up, acceleration, and other factors dependent on volatility, even that relating to alcohol blends, has been carried out in the United States and is reviewed in the article on Motor Fuels in the United States, p. 2395.

A certain amount of work has been carried out on volatility indices, such as that of Ostwald [13, 1925, 1927], but as these are not based on any practical background they are of relatively little value. (see also Kroch [7, 1926].) The work of Hoffert and Claxton indicated that the normal correlation of ease of starting with the percentage evaporated at the 70° C. or the 10% evaporated point which holds for gasolines is not correct for benzol mixtures, and such mixtures enable easier starting than would be indicated by this factor [5, 1933].

A comparison of the trend in compression ratios of British, Continental, and American automobile engines from 1929 to 1936 (see Fig. 1) [2], shows that the tendency for compression ratios to increase is the same in all countries. It will be noted that sports cars have very high compression ratios compared with normal types and, accordingly, these engines require fuels of high octane number. The high octane number fuels are increasingly being met by the use of lead tetra ethyl as an anti-knock agent, and in contrast with the single brand of this fuel available in the United Kingdom in 1927, in 1937 there were five brands of ethylized fuel on the British market. Motor fuels containing lead tetra ethyl are marketed in most European countries, but in Denmark the so-called Q grade containing less than 1·5 c.c. of lead per U.S. gallon and having an octane number of 70 is marketed.

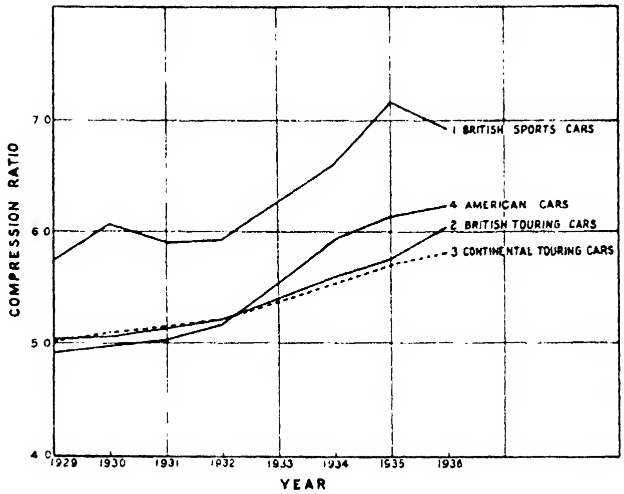


FIG. 1. Graph illustrating change in average compression ratio from 1929 to 1936.

An alternative anti-knock agent, iron carbonyl, was introduced in Germany, but proved to be unsatisfactory owing to its instability and its tendency to form deposits, especially on sparking-plugs.

Table I shows how octane numbers have increased during the last fourteen years. The figures quoted are by the C.F.R. research method, or, in the case of the earlier figures, they are obtained by conversion [20, 1932].

TABLE I

Octane Number C.F.R. Engine, Research Method

Years	*No. 1 Grade*	*No. 3 Grade*
1922	51	43
1925	55	53
1928	58	55
1931	68	61
1934	69	65
1936	70	66

Viewing the world's power and fuel problem with special reference to automotive traction [13, 1925, 1927], (1) the relatively low proportion of motor-cars to population is noteworthy for other countries in comparison with the United States (Table II) [1, 1936, 1937]; (2) native or indigenous supplies of fuel are unequally distributed. From the first fact it appears that the world demand for motor vehicles must eventually attain greater proportions, and consequently the use of automotive fuels must also expand; from the second fact the tendency exists for densely populated centres of civilization having little or no native supplies of petroleum, in unsettled international conditions, to make every effort to be independent of supplies from abroad. Two policies prevail in many continental countries: encouraging of home refining of imported crude, and the use of home-produced fuels other than petroleum products.

TABLE II

European Vehicle Registrations and Population, 1936

Country	*Cars*	*Other vehicles*	*Population*	*Consumption, gasoline Gals.*	*Gal./vehicle, approx.*†	*Population/vehicle*
Albania	510	820	1,000,000	..	..	800
Austria	27,452	73,895*	6,760,000	31,850,000	314	67
Belgium	124,183	135,252	8,250,000	88,200,000	340	32
Bulgaria	2,000	3,725	6,000,000	..	..	1,050
Czechoslovakia	77,569	75,957	14,730,000	65,800,000	428	96
Denmark	95,318	67,341	3,560,000	77,000,000	473	22
Esthonia	2,100	2,900	1,116,000	..	..	200
Finland	20,500	20,350	3,670,000	20,300,000	496	89
France	1,600,000	500,000*	42,000,000	805,000,000	383	20
Germany	945,085	1,482,080	66,000,000	595,000,000	245	27
Great Britain	1,604,948	1,002,163	44,500,000	1,347,500,000	516	17
Greece	7,500	7,550	6,200,000	12,950,000	806	400
Hungary	10,950	13,750	8,700,000	14,700,000	595	352
Irish Free State	45,211	14,337	3,000,000	38,850,000	652	50
Italy	290,000	270,000	43,000,000	157,500,000	281	77
Netherlands	90,100	101,900	8,000,000	121,800,000	634	42
Norway	42,321	39,342	2,810,000	41,650,000	510	34
Poland	19,000	16,900	32,150,000	33,950,000	946‡	1,230
Portugal	30,050	15,850	7,000,000	21,000,000	457	152
Roumania	17,500	8,750	18,000,000	27,650,000	1,053‡	700
Sweden	116,700	98,000	6,150,000	121,800,000	567	28
Switzerland	70,662	56,684	4,100,000	64,050,000	503	32
Yugo-Slavia	8,844	7,753	14,000,000	..	..	824

* Motor-trucks only.

† The consumption in gallons/vehicle is, of course, related to the proportion of other vehicles, e.g. motor-cycles having relatively low consumptions.

‡ Producing and Refining Countries.

For purposes of comparison, the number of vehicles registered in the U.S.A. (1936) is 28,086,380, which, compared with the total population of 137,000,000, gives a population/vehicle ratio of 5 : 1.

Table III shows the extent to which the use of substitute fuels was carried on in European countries in 1935 [21]. It will be seen that Germany is by far the greatest producer of substitute fuels in Europe. Table V shows the tonnage of imported gasoline in European countries over a period of years.

TABLE III

Consumption of Light Motor Fuels in European Countries, 1935

Country	*Total light fuels, tons*	*Total substitute fuels, tons*	*% of consumption*
Great Britain	4,400,000	292,000	6·6
France	2,685,000	355,000	13·2
Germany	1,930,000	855,000	44·3
Italy	501,000	16,000	3·2
Spain	436,000	13,000	3·0
Sweden	410,000	14,000	3·4
Holland	400,000	4,000	1·0
Belgium	360,000	8,000	2·2
Denmark	268,000	..	..
Switzerland	219,000	..	..
Czechoslovakia	235,000	51,000	21·7
Austria	143,000	10,000	7·0

Types of Substitute Fuels

The most common substitutes for petroleum spirit in use are alcohol and benzol. The use of coal spirits produced by low-temperature carbonization and hydrogenation is increasing, and similarly in some countries, notably Italy and Germany, the use of compressed gas and gas generators. The commonest form of gas generator in practice in these countries uses wood or wood charcoal as the gas producer.

The extent to which alcohol is used as a petroleum substitute is indicated by the consumption figures for European countries in Table IV [22, 1936]. The motor spirit produced from coal by hydrogenation or other methods is usually manufactured to the same specifications as imported motor spirit.

TABLE IV

Alcohol used as Motor Fuel in European Countries

Year	*Metric tons*	*Gallons*
1930	58,700	19,376,000
1931	121,000	39,964,000
1932	182,270	60,195,000
1933	361,650	119,435,000
1934	445,340	147,074,000
1935	576,448	191,381,000

Financial Aspect of Petroleum Substitutes

Owing to the relatively low price at which it is possible to import gasoline, European Governments draw very large revenues from the imposition of import duties and inland tax on this commodity. It is only when gasoline is taxed to the extent common in Europe that it is possible to produce substitutes such as alcohol and benzol at a competitive price. This means that in countries where legislation is enforced to encourage the use of these substitutes the Government has to buy the commodity from the producer and sell to the distributor at a loss in order to keep the price sufficiently low to satisfy the general public. In addition, the import and inland tax on the quantity of gasoline replaced by substitutes is lost. It has been estimated that, in France, a loss to the Government of 4,000 million francs (£40,000,000) has been incurred between 1923 and 1935. Similarly in Germany and Sweden it is estimated that the total loss to the State in 1935 amounted to 153 million Reichmarks (£8,000,000), and 3,800,000 Kr. (£200,000) respectively [22, 1936].

TABLE V [9, 1936]

Imports of Motor Spirit into European Countries over a period of years (in long tons)

Country	*1930*	*1931*	*1932*	*1933*	*1934*	*1935*	*1936*
United Kingdom	3,038,958	2,878,309	3,071,645	3,499,791	3,673,524	4,115,124	4,256,109
Irish Free State	105,720	130,791	98,924	105,903	113,759	..	..
Austria	108,278	83,147	59,646	48,849	47,547	60,606	..
Belgium	216,890	243,207	316,000	227,376	261,287	281,224	..
Denmark	203,868	238,583	231,305	215,145	252,389	253,188	257,400
Finland	92,251	55,795	28,048	59,201	67,387	..	..
France	1,865,284	2,130,797	1,978,651	1,714,792	1,041,546	574,821	..
Germany	1,412,011	1,325,389	1,070,500	988,890	1,140,090	1,217,502	..
Greece	46,791	48,978	46,488	45,548	41,265	54,522	..
Hungary	9,835	3,484	1,400	352	459	..	..
Italy	383,615	361,336	319,809	286,677	342,658	..	..
Holland	258,728	378,917	320,874	368,525	330,253	367,146	336,258
Norway	85,066	86,189	115,534	96,702	105,997	138,294	..
Poland	544	7	12	23	28	..	..
Roumania	10	57	nil	nil	nil	nil	..
Sweden	297,077	311,007	327,557	323,598	346,308	391,950	..
Switzerland	156,378	179,021	201,029	192,340	215,095	205,803	..

TABLE VI

Comparison of Motor Spirit Tests in Great Britain, 1927, 1932, and 1936

Grade	*Ethyl*			*No. 1*			*No. 3*			*Benzol Mixture*		
Year	*1936*	*1932*	*1927*	*1936*	*1932*	*1927*	*1936*	*1932*	*1927*	*1936*	*1932*	*1927*
Sp. gr.	0·738	0·735	0·739	0·733	0·735	0·734	0·747	0·737	0·735	0·784	0·777	0·774
Engler Distillation:												
I.B.P. °C.	38	34	46	35	34	39	40	35	41	51	50	50
% at 60° C.	9	10	2½	10	10	5	8	8	3½	2	2	½
70° C.	16	15½	8½	17½	16	11	14	13	8	9	6½	2½
80° C.	23	22½	16½	25	22½	19	20	19	15	23	17½	13½
90° C.	30½	30	25	32½	30	27½	26	26	22½	42½	33	28
100° C.	38½	38½	35	40	38½	37½	33	33	31½	58	50	43½
120° C.	57	60	54½	58	55½	58½	43	50½	50½	73	70	62½
140° C.	73	78	75	73½	72	77	57½	68	70½	83	80	75
160° C.	86	88½	88	87½	83½	88½	72	82½	87	90½	90	85
180° C.	95½	96	96	94½	93	96½	87½	91	95	97	96½	93
End Pt. °C.	185	185	186	185	196	183	201	205	186	190	187	199
Octane no.	81	77	72	70	69½	63	66	65	58	70	69	65

United Kingdom

The imports of gasoline into the United Kingdom have reached a high figure (Table V), and the production of substitute fuels forms only a very small proportion of the total consumption in the United Kingdom. The consumption of power alcohol has risen from 842,383 gallons in 1935 to 2,274,049 gallons in 1936 [14, 1937]. Motor benzole consumed in 1935 amounted to 42,250,000 gallons, and this figure was considerably increased in 1936. Motor spirits from shales and low-temperature carbonization of coal amounted to 10,950,000 gallons in 1935, and the output remains approximately the same in 1936. Hydrogenated spirit rose in output from nil in 1934 to some 20¾ million gallons in 1935 and 33,600,000 gallons in 1936.

Alcohol blends can be sold at the same price as ordinary first-grade gasoline by reason of the fact that under the Finance Act, 1921, alcohol used in internal combustion engines, provided it is blended with a minimum of 25% gasoline or benzol, is tax free and, under the Revenue Act of 1906, home-produced alcohol for use in road vehicles also receives a drawback of 8¾*d.* per imperial gallon, whereas gasoline, either imported or home refined from imported crude petroleum, is taxed at 8*d.* per gallon. Benzole mixtures are sold in Great Britain by three companies. Some idea of the improvements that have taken place in the quality of motor spirit sold on the British market can be gained from Table VI, showing tests on typical grades of motor spirits over a number of years. The improvements in octane number and volatility, to meet the use of higher compression ratios, and the demand for easy starting, are noteworthy [25].

Fiscal Definition.

The Government Light Oil Specification which governs gasoline taxation is broadly defined and includes white spirits, and other products not intended for use in motors, which are, however, taxed as gasoline. The specification defines the product as a hydrocarbon oil of which not less than 50% by volume distils at a temperature not exceeding 185° C., or of which not less than 95% by volume distils at a temperature not exceeding 240° C., or which gives off an inflammable vapour at a temperature of less than 22·8° C.

Irish Free State

The policy of the Government is to encourage the domestic refining of imported crudes, and the encouragement of the manufacture of power alcohol is part of the self-sufficiency programme that the State has adopted. The estimated production of alcohol during 1937 is 1,000,000 gallons and the price to be charged to fuel distributors is said to be 3*s.* 6*d.* per gallon comparing with 1*s.* 8*d.* per gallon for first-grade gasoline. The Irish Industrial Distributors' Association has come to an agreement with the Government to confine the sale of the alcohol mixture to the bigger transport companies, who will absorb the entire output [15, 1936].

The Irish Government is endeavouring to foster the refining of crude petroleum. Since there is no crude petroleum production in Ireland, any refinery is dependent on outside sources for its raw material, and, furthermore, to obtain grades of petroleum products approaching the standard of quality at present enjoyed by Irish consumers, and in the relative quantities required, involves the refining and blending of crudes from many entirely different parts of the world [16, 1937].

Continental Europe

In many of the countries of Continental Europe there are fiscal specifications distinguishing between motor fuels and higher boiling products such as kerosines and gas oils, and reference is made to some of these under the separate countries. These specifications are, however, changed from time to time. Premium and regular grade motor fuels are sold in practically all countries, differing chiefly in octane number. In general, apart from alcohol blends, the specifications of motor fuels are essentially similar in all continental countries.

France

The policy adopted by France is one of home refining of imported crude for gasoline supplies. This refining policy is backed up with fourteen thoroughly modern refineries with a capacity of over 6,000,000 tons of crude per annum [26, 1935].

France is by far the largest power alcohol consuming country in the world, which was the result, in the first place, of huge surplus stocks of alcohol being available after the War. However, the industrial demands in France for alcohol for rearmaments, and for export, have increased considerably of late, and the production of power alcohol was rather reduced in 1936. It is consequently expected that the quantity of power alcohol that is likely to be available during 1937 will be some 30% short of that available during 1936.

Originally, the distributors were compelled to market a 'Carburant National' consisting of approximately 50% alcohol and 50% gasoline. This mixture was unpopular with the public, and the chief and practically sole users were Government departments and Paris omnibus services.

In October 1931 a law was passed making it obligatory to sell all heavy gasoline in a mixture of 25 to 35 litres of alcohol to 100 litres of gasoline. This mixture is known as 'Carburant Poids Lourd'. It was found, however, that distributors could not dispose of their total commitments through this channel, and in February 1933 a decree was published which authorized the addition of alcohol to first-grade gasoline (essence tourisme) in the proportion of from 15 to 25 volumes of alcohol to 100 volumes of gasoline, but a few months later this was altered to 11 to 15 volumes of alcohol to 100 volumes gasoline. Many distributors now add from 10 to 15% of alcohol to their first-grade gasoline.

The following table shows the growth in annual alcohol yield over a period of years [3, 1935]:

Year	*Hectolitres*
1924/5	2,000,000
1925/6	1,553,760
1926/7	1,416,616
1927/8	2,112,207
1928/9	2,171,819
1929/30	3,000,000
1930/1	3,092,892
1931/2	3,314,991
1932/3	4,262,121
1933/4	4,000,000
1934/5	4,800,000

A recent decree also provides for synthetic fuels, and states that holders of petroleum import permits will, in proportion to their imports of similar products involved, bear the cost of forming and running a 'comptoir' for the disposal of the synthetic products, and the price at which these products will be unloaded on the 'comptoir', their allocation, and the prices at which they will be disposed of are to be fixed by the Government.

Since France is a great importer of coal, little development is taking place in low-temperature carbonization of this product, although lignite is a promising raw material.

The fiscal definitions of motor spirits, according to the decree of 29 May 1935 are:

Essence. Products distilling at least 15% by volume below 100° C., and at least 95% below 215° C., including losses, employing the normal method of distillation.

Essence Tourisme. This is defined as a clear, neutral spirit, not containing sulphur when tested by the Doctor method, not giving rise to deposits, and responding to the conditions below, based on the A.S.T.M. distillation test.

(1) At least 30% by volume to distil over below 100° C., and at least 95% below 185° C., including losses.

(2) The Final Boiling-point shall not be greater than 205° C., and the residue shall not be more than 2%, and shall remain liquid at a temperature of 15° C.

Germany

Although the domestic production of crude petroleum in Germany has increased considerably in the last few years, due to intensive exploration and development work, it still remains small, and there are poor prospects of its attaining pronounced importance. In 1935 domestic crude furnished only around 5% of the national requirements of gasoline [12, 1937].

TABLE VII

Germany's Production of Crude Petroleum

Year	*Quantity (metric tons)*
1928	92,000
1929	103,800
1930	174,000
1931	229,000
1932	230,000
1933	239,000
1934	320,000
1935	430,000

Germany's domestic supply of benzol has been increased by various means. One has been the installation of improved equipment in coke plants, particularly the 'Still' inner suction process, enabling a higher yield of tar and benzol per unit of coal processed.

In recent years alcohol has become a very important factor in the German motor fuel market. Faced with the constant increase in the stocks of alcohol, the Government directed their attention to assisting the distilleries and, indirectly, the farmer, by creating new outlets for alcohol. In August 1930 a decree was issued making it compulsory for importers and domestic manufacturers of gasoline to purchase a certain amount of alcohol from the German Federal Alcohol Monopoly. By this decree alcohol was to be purchased at the rate of 2½% of the net weight of all gasoline imported or purchased within the country, but the ratio has increased gradually until it has reached 10%. Later, owing to the shortness of supplies of potatoes available for the manufacture of alcohol, difficulty has been experienced in supplying the quantities required. On the other hand, the synthetic production of methyl alcohol has increased considerably, and, moreover, this can be produced at a lower cost than ethyl alcohol from potatoes. As a result of this, two new regulations appeared in the latter end of 1936: one stipulating that motor benzole may be sold in the open markets only if it contains one part by weight of methanol for every ten parts of benzole, and that ethyl alcohol used in motor fuel shall be mixed with methyl alcohol in the proportion of 4 to 1 respectively. The second regulation prohibits the use of motor fuel which contains no alcohol; the alcohol-free zones are abolished, so that the same kind of motor fuel is now available throughout Germany [17, 1936]. On 1 May 1937 a new regulation came into force stipulating that premium grade gasolines may be sold free from alcohol, while the regular grades must contain 13 to 16% by weight of alcohol consisting of two parts ethyl alcohol and one part methyl alcohol by weight.

It is of interest to note that it has been reported that this recent decree regarding methanol has caused trouble to engine-builders [4, 1936]. Methanol has been found to corrode the light magnesium-zinc-aluminium alloys forming magnesium methylate, and this action is said to be more pronounced in a gasoline mixture than in the pure methanol. Iron and lead-coated iron are attacked, and even galvanized iron is stripped of its coating of zinc. The question of just what changes must be made in the composition of metal alloys used by the engine-builders still awaits completion of further investigations.

The following figures for the home production of gasoline, benzol, and alcohol afford an interesting comparison with the petroleum import figures in Table V [18, 1935].

	1934	*1935*
Gasoline	*Tons*	*Tons*
Domestic production . . .	250,000	365,000
Benzole		
Domestic production . . .	280,000	380,000
Imports	70,000	40,000
Alcohol		
Domestic production . . .	170,000	180,000

The production of petrol from coal and lignite by hydrogenation and low-temperature carbonization has received much attention, and the estimated total production from plants operating in 1935, under construction or projected, was 885,000 to 945,000 tons per annum [23, 1935]. Lignite is the predominating raw material, and the home production of petrol from this source has been strenuously developed. The present programme (1937) anticipates that within fifteen months Germany will be able to manufacture the whole supplies of motor spirit required from indigenous sources.

Considerable work has also been carried out in Germany in the use of gas for motor vehicles, both town gas and gas generated on the vehicle from wood charcoal and similar substances. In order to carry a satisfactory supply of town gas for an internal combustion engine, it has to be highly compressed, figures of 2,250 lb. per sq. in. being common [11]. Using a new steel alloy, cylinders are constructed which can stand 200 atm. pressure, and are sufficiently light to attach to a truck. The gas is fed to the motor through two pressure-reducing valves, and very satisfactory operation has been claimed [6, 1936]. Numerous town-gas filling-stations have been established in Hanover and Berlin, and many others are under construction throughout the country.

Tests were carried out in 1936 on a fleet of 46 trucks, 38 of which were equipped with gas producer and explosion engines, including 20 operating on wood, 1 on low-temperature brown coal coke, 10 on wood charcoal, 2 on anthracite, 2 on peat coke, 1 on brown coal briquettes, and 2 on low-temperature coke. Of the remaining 8 vehicles, 3 were operated on Diesel oil from brown coal, 1 on rich gas, 1 on methanol, and the remaining 2 were equipped with steam-engines [10]. Trucks carrying full loads were driven over a course of 16,000 km., including all grades and traffic conditions. It was found that brown coal coke, stone coal coke, and anthracite gave the lowest fuel cost. Travel speed with liquid fuels was much greater than with producer gas, and the latter required a somewhat more expensive servicing. The motors operating on generator gas required more time for starting, whether hot or cold. Cylinder wear was stated to be no greater with wood or wood charcoal than with Diesel motors, which testifies to the efficiency of the gas filtering systems. The different fuels had quite different effects on lubricating oil. Wood fuel produces tar which tends to increase viscosity, acidity, and asphalt content. Compressed gas and methanol gave the least oil contamination.

Italy

The policy adopted in Italy is that of encouraging the use of substitute fuels wherever possible, and replacing imported gasoline by gasoline manufactured in Italian refineries from imported crude. Home refining has recently been extensively developed, although the home production of crude oil is very small, and the refining programme contemplates a capacity of from 1,000,000 to 1,200,000 tons of crude per annum. It is estimated that, to satisfy all requirements, upward of 2,000,000 tons of crude would have to be processed each year [27, 1935].

Efforts are also being made to increase the national production of ethyl and methyl alcohol. The Royal decree-law No. 1965 of 7 November 1935 fixed a remunerative price for root alcohol and stipulated for its admixture with imported or home-produced gasoline. Steps have also been taken to effect an ultimate increase in the production of benzole and other special motor fuels. The Italian Government aims at making it possible within three years to add 20% of alcohol to all gasolines consumed.

Amongst laws enacted with the object of rendering Italy as soon, and as much, as possible independent of foreign motor fuels is the substitute fuel decree announced at Bolzano at the end of August 1935 in the following terms:

> 'The Council of Ministers has approved a decree-law stipulating that all publicly or privately owned motor vehicles employed for collective passenger transport, urban or interurban, shall be run by means of gas-generating motors or on substitute fuels. The conversion of such motor vehicles at present in service must be effected by 31 December 1937.'

Much experimental work has been carried out in Italy with gas-generating sets for motor vehicles, and every encouragement is given by the Government for the utilization of this type of fuel. Hydrogenation is also being developed in Italy, and it has been shown that the lignites of Tuscany can be hydrogenated with a direct yield of about 15% of good gasoline, and 30% of total liquid oil [8].

All liquid motor fuels of the gasoline type in Italy contain alcohol or a mixture of alcohol and benzole.

Sweden

The Swedish Government has, during the last few years, taken steps to foster the use of home-produced motor fuel, being led thereto partly in order to assist the distilling industry, and to alleviate the distress caused by the low prices of agricultural products. In August 1931 the Government issued instructions to all Government departments to give preference to home-produced motor fuel, provided that its cost did not exceed that of imported fuel by more than 10%.

Having regard to the Government's wish to encourage the use of home-produced fuel, the leading oil companies voluntarily agreed to take over the surplus alcohol production from sulphite pulp in the paper industry. The alcohol was sold by the gasoline distributors in a blended fuel known as Lattbentyl, consisting of 25% alcohol and 75% gasoline.

In July 1934 a Royal decree, coming into force in October 1934, was promulgated with the object of increasing the use of alcohol as a motor fuel. The Spritcentralen was obliged to purchase at a fixed price sulphite spirit up to a maximum of 40,000,000 litres per year. In order to provide a steady outlet for the stocks held by the Spritcentralen, distributors and manufacturers of motor spirit were obliged to acquire alcohol from this source.

The quantity of alcohol taken over by motor fuel distributors was fixed by the Government as from 1 October 1936 at 3·3% of the total imports of motor spirit [34, 1937].

Denmark

The use of alcohol in motor fuels in Denmark has been thoroughly investigated by a committee of the Royal Danish Agricultural Society. The report issued by this committee stated that the difficulty arising from the use of alcohol lies in the question of price, and that even were alcohol exempt from taxation it could not compete with gasoline, although a tax of 13 ore per litre (6·3*d*. per gallon) is levied on the latter. The admixture of 25% alcohol with gasoline would entail a total additional expenditure of 30·6 million crowns (£1,366,000) [24, 1937]. Stress was laid upon the increased transport expenses the farmers would have to incur as the result of the adoption of an alcohol policy, and the report reached the conclusion that unless gasoline prices in Denmark were considerably increased the question of alcohol mixtures did not merit serious consideration.

With the exception of a limited amount of motor benzole which is imported and used for racing machines, there is no appreciable consumption of any types of motor fuel other than petroleum products.

Holland

A committee appointed by the Dutch Government has decided that a policy aimed at increasing the production of power alcohol from beet sugar for incorporation with gasoline would mean a lowering of the quality of motor fuel at present enjoyed by the consumer, would increase its cost, and would, moreover, involve the Government in considerably more than the expenditure on the present subsidy to the beet-sugar industry [30, 1936].

Benzole is admixed with gasoline in one or two of the premium grades of motor spirit marketed in Holland, but, in general, petroleum products are used.

Switzerland

In the early part of 1936 the Swiss Government modified the Alcohol Law with the object of overcoming the deficit of the Government Alcohol Administration, and, as a remedial measure, made compulsory the admixture of alcohol with gasoline. As a result of this decree, the Swiss Federal Council purchased 37,740 barrels of alcohol from distillers for re-sale and use in alcohol-gasoline motor fuel. The cost was £705,400, but in order to keep the blended fuel competitive in price with straight gasoline the alcohol was sold for £254,200 causing the Government to lose £451,200. Processing costs and loss of import duties on gasoline increased the Government losses to an estimated total of £647,200 [19, 1936].

The Government's plan contemplated that Swiss motorists would pay an additional centime per litre for their gasoline, an added cost which would have increased their total fuel bill by about £176,400, but it now appears that this will be changed owing to the unpopularity of this policy.

Regular grades of motor spirit in Switzerland are, in the main, petroleum products, but both alcohol and benzole are also admixed in some of the premium grades.

Austria

Austria is a non-producer of crude petroleum, and imports, mainly from Roumania, the requirements of its seven refineries. The plants produce only about 30% of the gasoline consumed in the country, the remainder being imported. Until 1931 benzole was the only other product which figured in this motor-fuel market, and was usually sold in a blend containing 40% of benzole and 60% of gasoline. The average yearly production of benzole used in this connexion amounted to about 25,000 barrels.

Following the passage of a law to regulate mixture of alcohol with motor fuel, passed on 1 February 1931, and becoming effective on 1 May 1931, alcohol became a factor in the Austrian fuel market. This law gave the Minister of Finance power to enforce the compulsory admixture of not more than 25% of alcohol of Austrian origin with gasoline, provided the price of the alcohol was not higher than the wholesale price of gasoline. This restrictive provision regarding the maximum price of alcohol has since been rescinded by a decree dated 9 September 1933.

On 7 July 1934 legislation came into force governing the distribution of alcohol. It was enacted that alcohol for the purpose of admixture must be of at least 99·5% purity and of Austrian manufacture. Importers of gasoline must purchase 2% alcohol by weight of the total gasoline imported and, in the case of the manufacturer of gasoline, 3·75% by weight of the total manufactured. The alcohol purchased must be used for the purpose of making a fuel mixture of which at least 20 and not more than 40 parts by weight must be alcohol, the rest to be gasoline, or gasoline and benzole.

Hungary

Owing to the overproduction of farm products, and of alcohol, a law came into effect in 1929 making it compulsory to mix all gasoline with a specific gravity of from 0·736 to 0·770 used for propelling motor vehicles, with anhydrous alcohol in such proportion that the resulting mixture contains 20% of alcohol. This, however, did not apply to gasoline used by motors in the agricultural industry. The alcohol, which must be not less than 99·5% pure, is purchased from the Agricultural Alcohol Trading Company, a State controlled cartel, which sells it to the oil companies at a price fixed from time to time by the Minister of Finance. Although petroleum spirit of lower specific gravity can be sold as such, the tax on it is more than double that on the heavier grade, so that alcohol blends are the most widely used in Hungary.

Roumania

Roumania is the second largest crude-producing country in Europe, and exports roughly 2,000,000 tons of gasoline annually; under present conditions this product is shipped to Constantza on the Black Sea by railway, the oil companies paying the railways (which are State controlled) about 430 lei per ton. Pipeline transportation is gradually being developed, the total length of pipeline laid up to 1935 being 3,360 km. The growth of this system of oil transport will materially assist the development of the oil industry in Roumania. Apart from external conditions, the oil industry has had to contend with high internal taxes, it being estimated that more than half the income of the Government is derived from oil.

TABLE VIII

Year	*Refining capacity (tons)*		*Crude production (tons)*
	Distilling	*Cracking*	
1930	6,800,000	765,000	5,744,000
1931	8,400,000	834,000	6,657,000
1932	9,080,000	985,000	7,350,000
1933	9,837,000	1,059,000	7,387,000
1934	10,574,000	1,354,000	8,472,000
1935	11,764,000	1,500,000	8,382,000

Most Roumanian crude is of paraffinic origin, and the straight gasolines produced are distinguished by low sulphur content and low octane number. A limited amount of naphthenic crude is produced and refined for the production of aviation gasolines.

The growth of cracking in the refining industry is illustrated in Table VIII [28, 1936].

Roumanian petroleum products are exported, principally, to Germany, Austria, Italy, Hungary, Czechoslovakia, Egypt, and the Near East, and the growth of the gasoline export trade can be seen from Table IX [29, 1937].

TABLE IX

Gasoline Exports

Year	*Tons*
1913	241,726
1929	802,421
1930	1,119,469
1931	1,547,472
1932	1,639,229
1933	1,757,216
1934	1,957,690
1935	1,951,922

Poland

The situation in Poland is different from the European countries other than Roumania in that there is a plentiful supply of Polish crude as a basis for motor requirements. The straight motor gasoline produced from Polish crude has rather a low octane number (60/61), but is of low sulphur content. However, a decree dated 11 July 1932 authorizes the Council of Ministers to compel the admixture of alcohol with gasoline. An agreement was reached with the Alcohol Monopoly whereby the oil companies purchased alcohol equivalent in quantity to 9% of their sales of gasoline during the previous year. As the consumption of gasoline in 1932 amounted to about 100,000,000 litres, the quantity of alcohol which had to be purchased during 1933 amounted to approximately 9,000,000 litres. It was provided that if, during any subsequent year, the consumption of gasoline was greater than in 1933, the alcohol quota would be increased by 2% for every 10% increase over and above the amount of gasoline consumed during 1933, with a further provision that at no time will the oil companies have to purchase alcohol equivalent to more than 30% of the previous year's sale of gasoline.

REFERENCES

1. *Automotive Industries*, **74** (8), 232 (1936); **76** (9), 272 (1937).
2. *Automotive Industries, Statistical Review*, **60–74** (1929–36).
3. Beatty, H. O. *World Petr.* **6,** 99 (1935).
4. Dietrich, K. R., and Lohrengel, W. *Oel u. Kohle*, **12** (5), 91 (1936).
5. Hoffert, W. H., and Claxton, G. *Engineering*, **135,** 300, 374 (1933).
6. Kahno, H. *Oel u. Kohle*, **12** (7), 141 (1936).
7. Kroch. *Petr. Z.* **22,** 1245 (1926).
8. Levi, M. G., and Padovani, C. *Rev. Ital. Petrolio*, **3** (7), 4.
9. Mineral Industry of British Empire and Foreign Countries, 1930-4, *International Petroleum Trade*, U.S. Bur. of Mines **5** (1936).
10. *Motorenbetrieb. u. Maschinen-Schmierung*, **9** (2) 2.
11. Muller, B. *Chem. Ztg.* **58** (101), 1020.
12. *Nat. Petr. News*, **29** (12), 82 (1937).
13. Ostwald, W. *Petr. Z.* **21,** 1323 (1925); **23,** 445 (1927).
14. *Petr. Times*, **37** (945), 247.
15. *Petr. Times*, **36** (928), 520.
16. *Petr. Times*, **37** (950), 401.
17. *Petr. Times*, **36** (917), 169.
18. *Petr. Times*, **35** (897), 378.
19. *Petr. Times*, **36** (924), 392.
20. Thorneycroft, O. C., and Ferguson, A. *J.I.F T.* **18,** 329 (1932).
21. Tokayer, O. *Petr. Press Service*, **3** (36), 281 (1 936).
22. —— *World Petr.* **7** (6), 309 (1936).
23. —— *Petr. Press Service*, **2** (2), 5 (1935).
24. Webster, H. *Petr. Times*, **37** (939), 42.
25. Whatmough, W. A. *Automobile Engineer*, **26**. 350), 395; **22** (290), 75; **22** (291), 114.
26. *World Petr.* **6,** 586 (1935).
27. *World Petr.* **6,** 592 (1935).
28. *World Petr.* **7** (10), 557 (1936).
29. *World Petr.* **8** (1), 44 (1937).
30. *Petr. Times*, **36** (907), 690.

NATURAL GASOLINE

By **GEORGE GRANGER BROWN, A.I.C.E.,** *Professor of Chemical Engineering,* and **DONALD L. KATZ,**
University of Michigan, Ann Arbor, Michigan

Introductory

NATURAL gasoline, frequently called 'natural gas gasoline' or 'casing-head gasoline', is a volatile, hydrocarbon liquid extracted from natural gas. It has properties somewhat similar to but is much more volatile than refinery gasoline. Inasmuch as natural gasoline is extracted from natural gas, the history of the natural gasoline industry is closely associated with that of the natural gas and crude oil industries.

In 1903 at Sistersville, West Virginia [25, 1922], and in 1904 at Tidioute, Pennsylvania, U.S.A. [7, 1925], the first commercial quantities of natural gasoline were extracted from natural gas by cooling the gas at pipeline pressures. The liquid condensate was 'weathered' to atmospheric pressure and sold as casing-head gasoline because the natural gas came from the casing-head of oil-wells. In 1905 compressors were used to raise the pressure of the gas during the cooling operation to increase the quantity condensed over that obtained at the natural gas line pressure. This operation was the beginning of the commercial compression process for natural gasoline manufacture.

The natural gasoline industry grew gradually at first, using the compression process to conserve a portion of the natural gas which was wasted or used as low-grade fuel and transform it into a valuable motor fuel. By the year 1915 natural gasoline production was equivalent to 0·7% of the crude oil production in the United States. At about this time the oil-absorption process of recovering natural gasoline began to gain favour, and by 1920 27% of the natural gasoline manufactured was extracted by this process. By 1928 about 86% of the natural gasoline production in the United States was by the oil-absorption method, which is the major process in commercial use.

For a few years following 1920 a small portion of the natural gasoline was produced by the charcoal adsorption process used alone or in conjunction with the oil-absorption process.

At the present time (1936) in the United States there are 840 natural gasoline plants having a rated daily capacity of 10,000,000 gallons raw or unstabilized gasoline, but with an average daily production of 4,500,000 gallons of finished gasoline. This quantity of gasoline is equivalent to 3·4% of the present U.S. crude production or 8·9% of the total gasoline manufactured (A.P.I. data). In 1930 the natural gasoline production, although no greater in net quantity, was equal to 12·5% of the total motor fuel. Natural gasoline is an important contributor to motor-fuel production and aids materially in reducing crude oil requirements for the motor-fuel market. The number of gasoline plants and their daily capacity is given in Table I [22, 1936].

The areas which produced natural gasoline are coincident with those which produced crude oil and natural gas. West Virginia and Pennsylvania were the initial leaders in production, but the leading position shifted to Oklahoma, California, and Texas, along with the discoveries of the crude oil and natural gasfields in those states. Part of the expansion of the industry was due to the large plants which were constructed at the site of the large pools of crude oil discovered. Thus one plant now produces 200,000 gallons of gasoline per day, a production equivalent to the combined capacity of some 400 plants operating in 1915.

The continual expansion of the natural gasoline industry into such fields as recovering propane and butane for polymerization processes is another step in conservation which brings it closer to the final goal of conserving all waste gases produced along with crude oil, and converting them into high-quality fuels.

TABLE I

Natural Gasoline Plants in U.S.A.

Year	*Number of plants*	*Daily capacity (U.S. gal.)*
1936	840	10,033,687
1935	850	9,909,797
1934	882	10,241,989
1933	919	10,308,354
1932	948	10,536,182
1931	987	10,531,511
1930	1,071	9,541,320
1929	1,124	8,695,727
1928	1,229	7,865,652
1927	1,148	6,947,264
1926	1,063	5,121,000
1925	1,143	4,642,561
1924	1,012	3,396,961

Source and Composition of Natural Gasoline

Natural gasoline is extracted from natural gas. Natural gas which carries gasoline is usually associated with crude oil. Natural gasoline is composed, then, of those constituents present in crude oil which vaporize in material quantities under the conditions of separation of crude oil and natural gas, provided they are not too volatile. A consideration of crude oil analyses and the conditions under which crude oil and natural gas are separated will explain the sources and compositions of natural gasoline.

Natural gas may be placed in five classes, depending upon the method by which it is separated from crude oil. These five classes of gas are all processed for natural gasoline and might be found in a single oilfield during its lifetime.

The first classification, represented by (*a*) of Fig. 1, is the 'casing-head gas' so frequently mentioned in the literature. The gas is removed from the crude oil in the reservoir before the oil enters the pump which lifts the oil to the surface. The gas travels from the reservoir to the surface of the earth in the annular space between the tubing and the casing. In many cases the gas leaving the casing-head may be under a vacuum due to the suction of the compressors on the gas-line, and is therefore frequently referred to as 'vacuum gas'. However, the oil and gas are not necessarily separated from each other at a pressure lower than atmospheric, but the pressure of separation is normally lower in these cases than in those which have no vacuum applied at the casing-head. The temperature of separation depends on the depth and geological area and is likely to be in the range 100–150° F. for most Mid-Continent fields.

The second classification is gas which is in solution with the crude oil or in the liquid state in the reservoir and is separated from the crude oil at the surface. If the reservoir pressure is high, greater than 25 lb. per 100 ft. depth, the wells of this type are likely to flow naturally and might be represented by (*b*) of Fig. 1. This surface separation of the oil and gas is carried on in 'separators' or 'traps'. The pressure of this separation is determined by the gas-line pressure and varies from atmospheric to about 75 lb. per sq. in. for low-pressure separations and from 150 to 400 lb. per sq. in. for high-pressure separations. The temperature of the separation depends on the reservoir temperature, the flow rate of the crude oil, and atmospheric temperature.

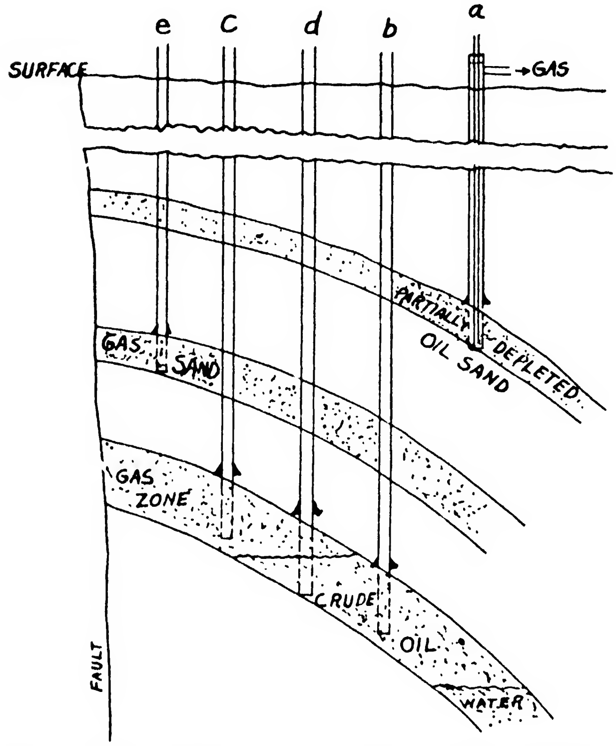


FIG. 1. Diagrammatic view of subsurface conditions of crude oil and natural gas.

The third class is gas produced from the gas phase of a reservoir which contains both gas and crude oil, as shown by (*c*) in Fig. 1. At the time the oil and gas reservoir is discovered, the gas and oil are in equilibrium at the reservoir pressure and temperature. As the reservoir pressure declines by oil and gas production, the gas phase may lose some of its heavier constituents by retrograde condensation and the gas in contact with the crude oil is likely to change composition to approach the changing equilibrium conditions. Therefore the gas which is produced from these 'gas-caps' of oilfields will have a relatively constant gasoline content unless some separation of liquid from the gas occurs at the well head previous to processing of the gas for natural gasoline. In such cases the gasoline content will vary with the temperature and pressure of this separation.

The fourth classification is a combination of the second (*b*) and third (*c*), in that the well produces from both the gas and the oil phases of the reservoir. This class might be represented by (*d*) of Fig. 1, or by any reservoir containing free gas in addition to dissolved gas in contact with each other. If the crude oil in case (*b*) were saturated with gas at the initial conditions of pressure and temperature as it is when a gas-cap is present, then it will eventually change from a well producing gas in solution to a well producing both free gas and gas in solution. The free gas as it leaves the reservoir will have a composition depending on crude oil composition, reservoir temperature, and reservoir pressure. However, as both the free gas and dissolved gas are in equilibrium with the crude oil at the surface-separation conditions, the gasoline content will depend on those conditions. Gas or air-lift operations would come under this classification, as would the majority of the gas produced in fields having 'flush' production.

The fifth classification is gas considered to be coming from a gas sand. It will have its initial composition throughout the life of the pool except for the retrograde condensation of high-boiling hydrocarbons in the sand with a drop in reservoir pressure, or for changes in any separation conditions at the surface which might be imposed on the gas previous to sending it to the recovery plant. The gas in this class is very similar to that of the third class (*c*), for usually gas which carries gasoline and is present in a so-called 'gas sand' either is in contact with a small amount of crude oil or has migrated to its structural position after having been in contact with crude oil.

These five classifications indicate that natural gas may be separated from the crude oil under various conditions as summarized in Table II. A knowledge of the geological area under consideration will narrow all ranges involving reservoir temperatures and pressures, and a consideration of any natural gasoline project would include measurements of the conditions of reservoir temperature and pressure.

TABLE II

Conditions of Separation of Crude Oil and Natural Gas

Example	*Temperature range, ° F.*	*Pressure range, lb. per sq. in. abs.*
(*a*) Casing-head gas	60–225	5–400
(*b*) Gas in solution with crude	30–150	12–400
(*c*) Reservoir gas in contact with crude oil	80–225	500–3,500
(*d*) Mixture of free and solution gas	30–130	12–400
(*e*) Gas from a gas sand	60–225	400–3,000

In addition to the conditions of separation the composition of the crude oil and (or) natural gas must be known along with the effect of temperature and pressure upon the equilibrium separation conditions. The analysis of the volatile constituents present in a crude oil saturated with natural gas at 120° F. and 3,000 lb. per sq. in. abs. is given by Table III. When the gas has been removed from solution until the crude has a vapour pressure of 12 lb. per sq. in. abs. at 120° F., the crude would have the composition shown in this table under the heading of 12·0 lb. Such actual crude analyses of reservoir crude taken from the Crescent Pool in Oklahoma was reported by Lindsly [13, 1936], and of crude taken from the Conroe Pool, Texas, by Sage and Lacey [20, 1935].

In order to use liquid analyses in calculating vaporizations or gas analyses and hence gasoline contents, it is necessary to have equilibrium between the vapour and liquid and to know the relationships at the conditions of the equilibrium. The two prerequisites for obtaining equilibrium are time and intimacy of contact. In the phase relationships between natural gas and crude oil in underground reservoirs the time element ensures a close approach to equilibrium between the phases. In surface separations in commercial oil-gas separators, the intimacy of contact due to the bubbles of gas found and the agitation of flow provides for equilibrium. These two methods of separating oil and gas account for most of the gas processed for natural gasoline. The vapour/liquid equilibrium constants for hydrocarbons discussed elsewhere by Brown and Souders [8, 1932] have proved very useful in eliminating the gross errors of Raoult's law for pressures up to 500 lb. Experimental determinations of equilibrium constants for a natural gas/crude oil system up to 3,000 lb. pressure are to be published in the near future [19] and will provide accurate data representing equilibrium between crude oil and natural gas at the high pressures.

The analyses of the gases which are in equilibrium with the crude oils of Table III are given in Table IV, which are the means of determining the equilibrium constants for the stated temperatures and pressures. The gallons of condensate of each constituent which would be obtained by complete condensation of 1,000 cu. ft. of gas measured at 14·7 lb. per sq. in. abs. and 60° F. are also given. The details of the analyses and conversions to gallons will be found elsewhere. The extreme differences in the two analyses are representative of extreme differences in conditions of separating crude oil and natural gas. A natural gas which is separated from a crude oil at 600–1,000 lb. per sq. in. will carry a higher concentration of methane and lower concentration of the less volatile components than the gas separated at 3,000 lb. This fact is due to the equilibrium constants approaching unity as the pressure approaches the critical pressure of the mixture.

If 1,000 cu. ft. of the two gases given in Table IV were condensed, the 3,000-lb. gas would yield 3·7 gallons of liquid and the 12-lb. gas 24·8 gallons of liquid, both exclusive of methane. However, propane and ethane are too volatile to be used as gasoline, and it is seldom possible to include all the butanes even when making gasoline of the highest vapour pressure marketed. If these two gases are considered on the basis of their content of butane-free natural gasoline, they will be found to contain 0·72 and 8·6 gallons per 1,000 cu. ft. respectively.

TABLE III

Analysis of Typical Mid-Continent Crudes [11]

	3,000 pounds			*12·0 pounds*		
Constituents	*Mol %*	*Wt. %*	*Approx. volume %*	*Mol %*	*Wt. %*	*Approx. volume %*
Methane .	41·7	7·0	18·3	0·1	0·008	0·02
Ethane . .	7·6	2·4	3·9	0·2	0·03	0·06
Propane .	6·4	3·0	4·2	1·2	0·26	0·46
Butanes . .	4·6	2·8	3·4	3·3	0·9	1·4
Pentanes .	3·2	2·4	2·7	4·8	1·7	2·3
Hexanes .	3·2	2·9	3·0	6·0	2·5	3·2
Remainder of crude oil .	33·3	79·5	64·4	84·4	94·6	92·5

TABLE IV

Analysis of Gases in Equilibrium with Crude Oils

Constituent	*Gas in equilibrium with 3,000 lb. crude mol fraction*	*U.S. gal. per 1,000 cu. ft.*	*Gas in equilibrium with 12·0 lb. crude mol fraction*	*U.S. gal. per 1,000 cu. ft.*
Methane .	0·873	. .	0·230	. .
Ethane .	0·063	1·6	0·116	2·9
Propane .	0·0312	0·9	0·216	6·0
Butanes .	0·0157	0·5	0·220	7·3
Pentanes .	0·0069	0·25	0·104	3·8
Hexanes .	0·0047	0·20	0·053	2·2
Heptanes and heavier .	0·0055	0·27	0·053	2·6

Natural gasoline extraction normally is regulated to remove as high a percentage of the pentanes as is practicable for any particular case. When removing substantially all the pentanes the percentage of butane recovered is considerably less than that of the pentane because of the higher volatility of the butane, but the quantity of butane so recovered in the gasoline is sufficient to give the product a vapour pressure of 26 lb. per sq. in. Butane-free natural gasoline, containing only pentanes and less volatile, usually has a vapour pressure at 100° F. of about 12 lb. per sq. in. Gasoline of 26-lb. vapour pressure usually contains about 25–35% of butanes. Therefore, the composition of gasoline of any specified vapour pressure can be estimated from the composition of the natural gas from which it is extracted.

The analyses of the butane-free natural gasoline produced from the natural gases of Table IV may be computed by dividing the mol percentage of pentanes, hexanes, and heptanes by their sum to obtain the mol percentage in the butane-free gasoline. A similar computation using gallons per 1,000 cu. ft. will give the volume percentage composition. Likewise, it is possible to predict the composition of gasolines of various vapour pressures by using the equilibrium constants or Raoult's law to indicate the quantity of butane required to bring the pentane and less volatile (heavier) portion up to the desired vapour pressure. The gasoline will consist of that quantity of butane and substantially all the pentanes, hexanes, &c.

A 'rule of thumb' method of estimating the liquid volume composition of average natural gasolines from the Mid-Continent fields is that the hexanes equal 50% of the pentanes, the heptanes equal 50% of the hexanes, and the octanes and heavier equal the heptanes. This rule along with the other approximations, that 26·0-lb. vapour-pressure gasoline usually contains 25–35% of butanes, and that substantially butane-free gasoline has a vapour pressure of 12·0 lb., will give a rough method of approximating the composition of natural gasoline of any vapour pressure as produced directly without removal of any intermediate constituents.

This 'rule' is supported by a study of crude oil analyses and the equilibrium constants for the ranges of temperature and pressure at which vaporization of the natural gasoline constituents occurs. Most crude oils contain slightly less pentane than hexane and have about equal hexane and heptane quantities. There are many exceptions to this generalization, but for those crudes which provide the bulk of the natural gasoline in the Mid-Continent the relationship is fairly reliable. The ratios of the equilibrium constants at the low-pressure surface-separation conditions are of the order of 5 to 2 to 1 for pentanes, hexanes, and heptanes. Therefore, the ratio of 4 to 2 to 1 for the pentane, hexane, and heptane in natural gasoline is quite logical because the pentane concentration in the crude is less than the hexane or heptane, and because complete extraction is not always obtained for the pentanes, while the hexanes and heavier are usually almost completely extracted from the gas.

The percentages of the various constituents have been given as pentanes, hexanes, &c., with no reference to whether they were normal paraffins or isomeric compounds. It should be mentioned that substantially all the hydrocarbons having 5 or less carbon atoms which are present in crude oil are paraffin hydrocarbons within the limits of accuracy of the analyses used. Iso-butane is present in the butanes to the extent of about 20–30% of the total butanes. Iso-pentane is always present and may vary in the range 25–60% of the total pentanes with 30% as an average value. These constituents are normally identified in the usual fractional analysis, but due to the lower order of accuracy of separating the closer boiling compounds, and due to a minor interest, until recently, published values are often given as total pentanes or total butanes. In analysing for the hexanes and heptanes, isomers are found to be present in the same order of magnitude as normal paraffin compounds, but are not usually reported due to difficulties of separation. In the hydrocarbons having 6 carbon atoms or more, ring compounds may be present. Benzene has been found in small quantities in Mid-Continent natural gasoline but, excepting special considerations, natural gasoline may be considered as having the properties of paraffin hydrocarbons.

No emphasis was made of the quantities of compounds present of higher molecular weight than octanes. In the normal low-pressure vaporization process the volatility of the compounds decreases rapidly with increasing molecular weight and, because their concentration in the crude oil is not higher than pentanes or hexanes, the quantity vaporized will taper off rapidly also. However, in those cases where vaporization occurs under pressures of 1,500–3,000 lb. per sq. in. a different condition exists. At these high pressures the volatility of the higher molecular weight compounds is very much increased due to the approach to the critical pressure of the mixture. Therefore, relatively high concentrations of compounds boiling from 300 to 600° F. may be present in vapours separated from crude oil at high pressures. As previously mentioned, gases of this nature may be subjected to a separation process at the surface of the earth and a liquid obtained by retrograde condensation occurring with the decrease in pressure. In those cases the natural gas carries material quantities of hydrocarbons of a boiling range too high to be used for natural gasoline.

Estimation of Natural Gasoline Reserves

Natural gasoline reserves are a primary consideration for any natural gasoline plant or project. Under the heading of reserves might come the ultimate production from a given oil-pool or portion thereof, the gasoline content of the gas, and the rate of production. Inasmuch as natural gasoline is produced in conjunction with natural gas or crude oil, its rate and quantity of production will be closely associated with the crude oil and natural gas industries. Any one interested in natural gasoline reserves must also consider reserves of crude oil and gas.

The first consideration of natural gasoline reserves for an oilfield or portion thereof is the source of supply of the natural gas from which the gasoline is to be extracted. The geology and reservoir condition are necessary for answering this question and showing which of the classes of gas mentioned previously will be the source of the natural gasoline. Once the source is known, the composition of the gas or crude oil along with the quantity present will indicate possible reserves of gasoline. Then definite operating conditions will set the reserves for that condition.

A discussion of the several classes of gas mentioned earlier will indicate the methods used for estimating natural gasoline reserves. The simplest case is that in which the gas carrying the gasoline comes from a gas sand or formation containing a negligible quantity of crude oil. A careful analysis of this gas or standard methods of obtaining gasoline content will give the gallons of natural gasoline which may be extracted per 1,000 cu. ft. of gas. The problem, then, is to determine the quantity of natural gas present in the geological structure under consideration.

There are two methods by which the natural gas reserves may be obtained. The first of these is a pressure-drop volumetric withdrawal method. It assumes a constant volume reservoir and calculates the total connected volume of the reservoir which contains gas and thereby the amount of gas present. For example, if a reservoir pressure dropped from 1,000 to 950 lb. per sq. in. abs. for a given gas production, the gas having a density of 0·65 and the reservoir a temperature of 130° F., the standard cu. ft. of gas present in 1 cu. ft. of reservoir pore space will be:

(at 1,000 lb.)

$$1\times\frac{T_0(460+60)}{T(460+130)}\times\frac{P(1{,}000)}{P_0(14\cdot7)}\times\frac{1}{\frac{PV}{RT}(0\cdot905)}=66\cdot3\text{ cu. ft.}$$

(at 950 lb.)

$$1\times\frac{460+60}{460+130}\times\frac{950}{14\cdot7}\times\frac{1}{0\cdot91}=62\cdot7\text{ cu. ft.}$$

The deviation of gases from ideal gases, PV/RT, is an important item in some cases and the value used was taken from Katz [12, 1936], who used the data of Sage, Lacey, and Schaafsma [21, 1934]. The difference between 66·3 and 62·7 or 3·6 cu. ft. of gas is the quantity of gas which was evolved by each cu. ft. of connected reservoir space. The natural gas produced from the pool divided by 3·6 gives the volume of the reservoir pore space, and when multiplied by 62·7 gives the gas present in the reservoir at 950 lb. pressure. The important considerations of this method are that gas-well pressures are measured at the surface and should be corrected for the head of the gas in the well to give the reservoir pressure. Also, equalization of pressure in the connected reservoir may be slow due to tight sands.

The other method of obtaining gas reserves is to find the volume and porosity of the sand containing the gas and then with temperature, pressure, and deviations from the ideal gas laws calculate the quantity of gas reserve. The volume of the sand is taken from geological data and the porosity must be measured on cores taken from several wells drilled in the field. Porosities will likely be in the range of 12–25% of the sand volume. The method must assume either that no liquid or a definite quantity of crude or water is present in the pore space. Gas reserves are usually reported as the gas which would be produced when the reservoir pressure drops to some low pressure such as 100 lb. per sq. in., below which it is often considered uneconomical to recover the gas.

In estimating the gasoline reserves for the gas which is dissolved in crude oil, the crude oil present must be estimated. The methods of estimating crude reserves include (1) that based on sand volume and porosity, (2) that based on the rate of decline of production of crude oil, and (3) that based on reservoir pressure drop and volumetric withdrawal [12, 1936]. These methods give the initial quantity of crude with dissolved gas which is present. An analysis of the crude or initial operating gas to oil ratios will give the quantity of gas present per barrel of crude oil either at the surface or in the formation. Although all the crude oil initially present is not produced, most of the dissolved gas will be brought to the earth's surface if the reservoir pressure drops upon crude production. Therefore the initial crude present in reservoir times the dissolved gas gives the natural gas to be produced. Gasoline reserves can then be estimated from the gasoline contents of the gas which vary over the life of the pool.

In the other three classes of gas the same or similar considerations will give the quantity of gas and gasoline to be produced from any pool. Because of the difficulties in obtaining many of the above data, the estimation of the reserves often requires many assumptions which are based on past experience. Also it is noted that these methods often require a certain quantity of crude oil or gas production in order to estimate the quantity remaining in the reservoir. The complete proving of a pool by the drill is often awaited in contemplating natural gasoline plants. The larger natural gasoline plants of the present day are constructed after reserves of crude oil and natural gas are proved and thus are able to operate under the smaller margin of profit given by present economical conditions.

Gasoline contents of natural gas play an important part in gasoline reserves and have received considerably more attention in the industry than the foregoing relationships of oil and gas reserves. Present practice is to analyse the gas being produced in the initial stages of development of a pool by charcoal adsorption tests [9; 18, 1924], by compression test-car tests [7, 1925], or by fractional analyses of the gas described elsewhere.

The charcoal adsorption test consists of passing a measured quantity of natural gas through 250 c.c. of activated charcoal to adsorb the natural gasoline constituents. The charcoal is carried to the laboratory in the adsorption tube, placed in a flask along with some mercury, and heated. The heat transferred by the mercury distils the natural gasoline adsorbed and the vapours are condensed at 32° F. The distillate collected is warmed to 60° F. and the volume measured and reported as gallons per 1,000 cu. ft. of natural gas tested using charcoal process.

The compression method consists of compressing a measured quantity of gas to a pressure in range of 50–250 lb. and cooling the compressed gas to give a condensate. The apparatus used is a compressor mounted at the rear of a motor-car with a power take-off from drive shaft to compressor. The compressed gas is cooled at 32° F. and the condensate is weathered to 60° F. before measuring the quantity of liquid. These gasoline contents are likewise reported as gallons per 1,000 cu. ft. using compression or 'test-car' process.

These two tests are widely used for determining gasoline contents used in gas-purchase contracts and are an important factor in estimating gasoline contents for new plants. However, because of the nature of the tests, only a partial separation is made of propane, &c., from the natural gasoline condensed and of pentanes, hexanes, &c., from vapours uncondensed. In cases of unusual propane and butane contents or on low gasoline contents these methods are very unreliable in predicting plant yields. However, the long experience with the test methods have shown most discrepancies which may arise, and 'plant factors' are used to convert these gasoline contents to actual plant yields. In general, 'plant factors' run from one to two when considering the 26-lb. vapour-pressure product as the plant product, and are estimated from the gravity of the gas and gasoline content reported.

L. S. Gregory [10, 1935] has developed an improved compression or test-car method of obtaining gasoline contents for use in estimating plant yields. He has added a fractionating column which may be used to fractionate the condensate obtained by compression using solid carbon dioxide as the cooling medium. The gases propane and lighter are removed by fractionation from the condensate, the butanes are fractionated off and measured, and the butane-free natural gasoline remains to be measured and tested.

The low-temperature fractionation of natural gases gives the gasoline contents as previously described. The method is rather expensive for routine tests, but is very useful in estimating plant yields to be obtained from a natural gas. The analyses show not only the natural gasoline, but allow the calculation of the quantities of ethane, propane, and butanes to be recovered along with the gasoline. In conjunction with gas analyses, analyses of crude oil for the natural gasoline constituents as shown in Table III are very useful. Crude oil analyses, natural gas analyses, equilibrium constants, and a knowledge of the separation conditions can be used to calculate the gasoline contents for the various methods of vaporization or separation of crude oil and natural gas which will take place over the life of the pool. This method has the advantage of being able to calculate effect of changing pressures or temperatures of separation on the gasoline content and allows the calculation of separations which are difficult to accomplish experimentally.

The effect of temperature and pressure on the gasoline content of gas separation from crude oil at the well head in a regular oil-gas separator is an important factor in predicting gasoline reserves. If gasoline contents are measured by charcoal tests or by fractional analyses, the pressure and temperature should be known. The gasoline contents will decrease with increasing pressure on the separator and with decreasing temperature, as would be shown by an inspection of the equilibrium constants. If gasoline contents are measured in the summer and the rate of flow of the well is low, the gasoline content in the winter will be considerably lower. The calculating of contents for various pressures and temperatures shows the effect which all possible variations of conditions can bring about. Fig. 2 shows a typical single-stage separation and the results of separating crude oil of the indicated composition (reported by Lindsly) [13, 1936] at 75 lb. per sq. in. abs. The separated crude oil having a vapour pressure of 75 lb. per sq. in. at the separation temperature is then allowed to vaporize further at atmospheric pressure in the crude oil stock tank with the results as indicated.

The gasoline present in the separator gas is dependent upon the separator pressure. Increasing the pressure up to 500–600 lb. per sq. in. decreases the gasoline content. However, one factor which is often overlooked is the natural gasoline which is vaporized from the crude oil as it enters the crude oil stock tank. Fig. 3, based on similar crude, is a plot of the natural gasoline evolved from the separator (curve I). The natural gasoline evolved from the crude oil stock tank at atmospheric pressure (curve II), and the total natural gasoline vaporized from a barrel of crude oil (curve III), is a function of the pressure on the separator. A minimum total vaporization in this case occurs at about 140 lb. per sq. in. abs.

If the gasoline content of the gas from the separator is plotted as a function of separator pressure, the curve would be similar to curve I of Fig. 3. But such a curve could not be used directly for computing the quantity of natural gasoline evolved in the separator as the quantity of gas varies with separator pressure.

The ultimate reserves of natural gasoline in an oil-pool or gas-pool are an integrated product of the gas to be produced and the gasoline content of the gas. Frequently results of one field are used by the 'rule of thumb' operations in the industry, to predict reserves of a new field, often using the same number of gallons of natural gasoline per barrel of crude oil produced. Comparisons of this type are absolutely unreliable unless the gas is of the same classifications in the two cases and the crudes contain substantially the same concentrations of butanes, pentanes, and hexanes.

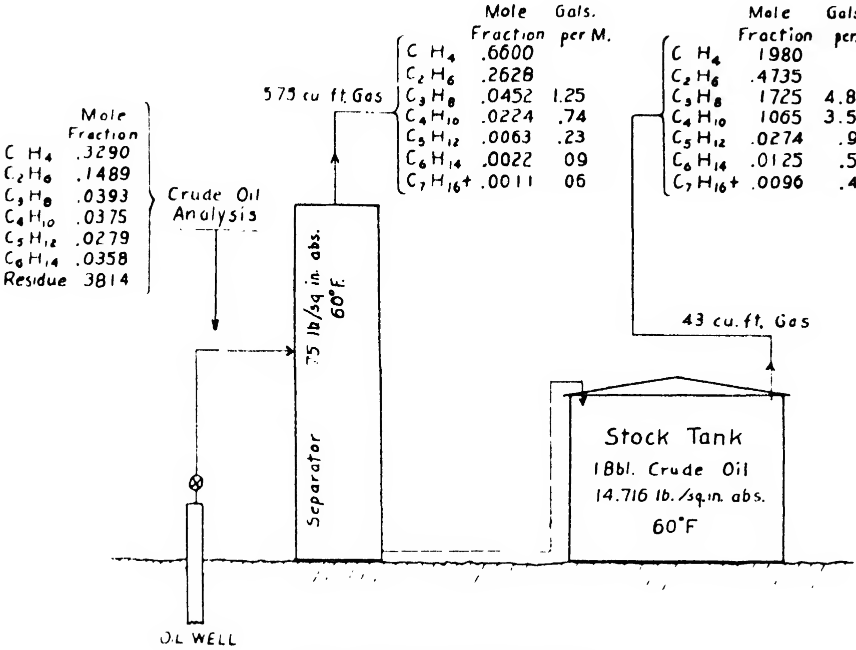


FIG. 2. Oil gas separation system.

Natural Gasoline Plants

In addition to determining natural gasoline reserves on a pool the contractual relations between the crude oil operator and the natural gasoline manufacturer must be satisfactory before the plant is constructed. In cases of unified ownership of crude or gas production this matter is simplified, but the bulk of the crude production in the United States is by diversified ownership of leases. The gasoline manufacturer contracts to meter and collect the natural gas from the crude oil–natural gas separation system, to return residue lean gas to the crude producer for fuel, and to pay a portion of the selling price of the gasoline extracted. Standard contracts have been prepared by the Natural Gasoline Association of America [14]. The crude producer receives about 15–30% of the selling price of the gasoline, getting a higher price for higher gasoline content gas based on a standard test such as the compression test car. In some cases the sellers of the natural gas receive a portion of the gasoline manufactured by the plant rather than an amount based on a content test. The average selling price of 26-lb. vapour-pressure gasoline during 1935 in the Mid-Continent was 3·3 cents.

As the gasoline manufacturer collects the gas and returns residue to the crude producer, a natural gasoline plant is considered as a gathering system, extraction system, residue lines, and gasoline stabilization or finishing equipment. Roughly one-half of the investment is in field lines and equipment for a normally distributed source of gas.

The oil-absorption process operating at pressures in the range of 30–500 lb. per sq. in. accounts for most of the production in the United States. The normal operation of a plant over the life of an oilfield consists of allowing the gas to come to the absorption system under its own pressure, then adding compressors to increase the capacity of the lines when the gas volumes exceed the capacity of the lines originally provided, and finally using compressors to raise low-pressure casing-head or separator gas to the desired extraction pressure. A complete discussion of the absorption process for gasoline recovery is given elsewhere (Barton). In addition to absorption plants, compression or combination compression plants are used. In case the residue gas is to be compressed for transmission, it is simpler to remove part of the gasoline by this process and then remove the uncondensed gasoline by an oil-scrubber. Residue gas from a compression plant often contains 0·4–0·5 gal. per thousand, and oil-absorption plants have been built to process 0·3 gal. per thousand natural gas.

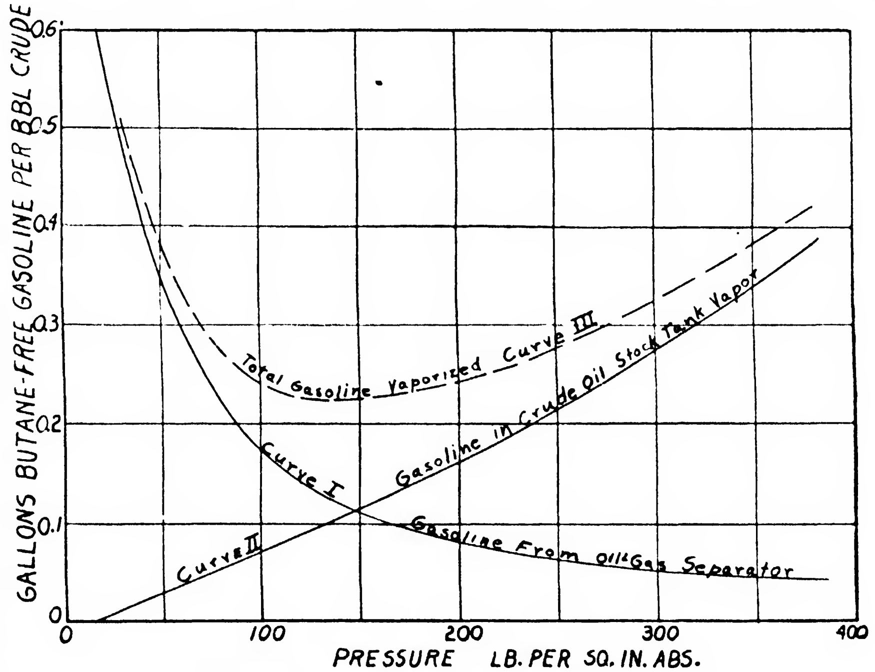


FIG. 3. Effect of pressure on natural gasoline content of gas.

A new method of recovering natural gasoline has been introduced in the past few years, high-pressure direct fractionation of the gas itself. At pressures above 200 lb., propane and butanes can be refluxed in a fractionating column using cooling water for condensation. Natural gases which contain enough propane, butane, and natural gasoline to give a condensate at these conditions of temperature and pressure and contain enough propane and butane to give the residue gas a dew-point at the conditions at the top of the fractionating tower without requiring pentane to be present can be treated advantageously in this manner. Only gases containing of the order of 50% or more of ethane and heavier are suitable for this process. The fractionating column takes the residue gas with as little pentane as possible overhead and the natural gasoline with as little propane as possible as kettle product. In those cases in which propane and butane are desirable for polymerization feed stock the recovery of those constituents may be included along with the natural gasoline.

In normal extraction processes, except direct fractionation, the raw gasoline produced contains the equilibrium amounts of propane, ethane, and methane which were extracted by virtue of their presence in the gas and their equilibrium distribution between the vapour and liquid. A portion of these volatile gases may be separated by venting the gases and reabsorption of the gasoline present. However, the major separation is carried on in fractionating columns called stabilizers. The normal procedure is to fractionate substantially all the methane, ethane, and propane from the gasoline and that portion of the butanes which will leave the desired vapour-pressure product. A more detailed discussion of these extractions and stabilization processes will be found under separate titles. Following the fractionation equipment, it may be necessary to sweeten the product in a manner similar to refining gasoline. The commercial products made are listed in Table V. The plant will make whatever product is to be sold, but in general will make lower vapour-pressure gasoline in spring and summer and the higher vapour-pressure gasolines in winter. The plant storage is generally pressure storage, and the bulk of the gasoline produced is moved to market by rail, boat, or pipeline shortly after production. In the loading of cars or boats, a vapour-recovery system removes hazard of fire and prevents losses of gasoline. If large quantities are to be stored, the lowest vapour-pressure gasolines are made and stored in standard 55,000-bbl. tanks equipped with vapour-recovery systems or floating roofs.

Special products are made by natural gasoline plants and will be treated as such.

TABLE V

Official Specifications and Testing Methods for Natural Gasoline. Effective 1 January 1932

Natural gasoline is a liquid petroleum product consisting of the heavy hydrocarbons extracted from natural gas by such means as compression, absorption, and other processes.

Natural gasoline is defined further for commercial purposes by the following specifications:

1. Reid vapour pressure—10–34 lb.
2. Percentage evaporated at 140° F.—25–85.
3. Percentage evaporated at 275° F.—Not less than 90.
4. End point—Not higher than 375° F.
5. Corrosion—Non-corrosive.
6. Doctor test—Negative, 'sweet'.
7. Colour—Not less than plus 25 (Saybolt).

In addition to the above general specifications natural gasoline shall be divided into 24 possible grades on a basis of vapour pressure and percentage evaporated at 140° F. Each grade shall have a range in vapour pressure of 4 lb., and a range in the percentage evaporated at 140° F. of 15%. The maximum vapour pressure of the various grades shall be 14, 18, 22, 26, 30, and 34 lb. respectively. The minimum percentage evaporated at 140° F. shall be 25, 40, 55, and 70 respectively. Each grade shall be designated by its maximum vapour pressure and its minimum percentage evaporated at 140° F., as shown in the accompanying table.

Grades of Natural Gasoline

Percentage evaporated at 140° F.

	25	40	55	70	85
34					
	Grade 34–25	Grade 34–40	Grade 34–55	Grade 34–70	
30					
	Grade 30–25	Grade 30–40	Grade 30–55	Grade 30–70	
26					
	Grade 26–25	Grade 26–40	Grade 26–55	Grade 26–70	
22					
	Grade 22–25	Grade 22–40	Grade 22–55	Grade 22–70	
18					
	Grade 18–25	Grade 18–40	Grade 18–55	Grade 18–70	
14					
	Grade 14–25	Grade 14–40	Grade 14–55	Grade 14–70	
10					

Testing Methods

Reid Vapour Pressure

Same as A.S.T.M. Method D. 323–31 T.

Corrosion Test

Same as A.S.T.M. Method D. 130–30.

Colour Test

Same as A.S.T.M. Method D. 156–23 T.

Distillation Test

Same as A.S.T.M. Method D. 216–32 T.

Complete description of apparatus can be found in 1932 standards of the American Society for Testing Materials, obtainable from the Society at 1315 Spruce Street, Philadelphia, Pa.

Utilization of Products

The primary use of natural gasoline is blending with refinery products to make motor fuel. However, in addition to regular motor fuel several special fuels and products come from natural gasoline plants, such as airplane fuels, solvents, polymerization feed stocks, and the liquefied petroleum gases.

Blending to make motor fuel from refinery gasoline and natural gasoline is controlled by three primary characteristics or specifications of the products: volatility, octane number, and vapour pressure. The volatility or extent to which a fuel will vaporize under any stated conditions is measured by the Engler or A.S.T.M. (American Society for Testing Materials test D. 86-35) distillation of the gasoline. Such points as 10, 30, 50, or 90% evaporated have been shown to have relationships to other properties or performance of the motor using the fuel. The octane number is determined by a test motor such as specified by the A.S.T.M. D. 357-34, and is related to detonating characteristics of the fuel for various compression pressures and temperatures. The vapour pressure as measured by the Reid vapour-pressure bomb, A.S.T.M. D. 417-35 T, represents the tendency of the fuel to form vapour. Vapour pressure is also related to the first portion of the distillation curve and may be estimated therefrom. The vapour pressure is related to the losses sustained in handling and 'vapour lock' in actual use in motor-cars. These three characteristics of pure hydrocarbons present in natural gasoline are given by Table VI.

The volatility of a motor fuel or of natural gasoline includes the entire distillation curve. Typical distillation curves are shown in Fig. 4, from the data of Trimble [23, 1933]. Other properties of the three fuels are shown by Table VII.

The A.S.T.M. distillations on mixtures of materials such as gasolines may be defined, except the initial and final portions, by a few points such as the 10, 50, and 90% points. Therefore, the temperature for any percentage evaporated on the distillation curve may be used as a measure of the temperatures over a range on the A.S.T.M. distillation. This fact has made it possible to relate certain characteristics of performance of fuels with a definite percentage evaporated for most gasolines.

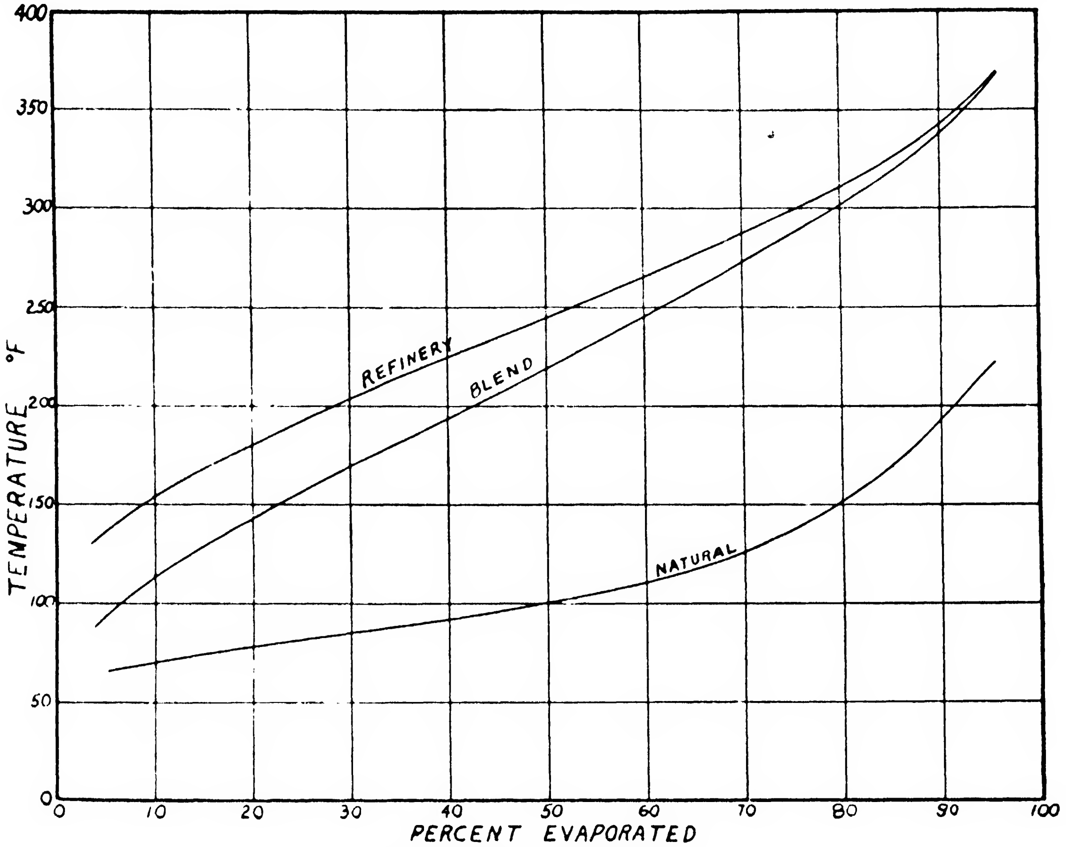


FIG. 4. Typical distillation curves.

TABLE VI

Properties of Natural Gasoline Hydrocarbons

Compound	*Octane no. A.S.T.M.* [15] *D. 357–33 T*	*Gravity, °API. at 60° F.*	*Vapour pressure at 100° F. lb. per sq. in. abs.*	*Boiling-point at 760 mm.* Hg, *° F.*
Propane	125	146·5	187	−44·1
Iso-butane	99	119·1	73·7	+10·0
n-Butane	91	110·6	52·2	+30·9
Iso-pentane	90	95·0	20·4	82·4
n-Pentane	64	92·7	15·6	96·8
n-Hexane	31*	81·6	4·9	155·7
n-Heptane	0	76·4	1·6	209·1
Iso-octane	100	71·8	..	210·7

* By interpolation.

TABLE VII

Properties of Gasolines

Gasoline	*°API.*	*Reid vapour pressure lb. per sq. in.*	*Octane no.*	
			A.S.T.M.	*C.F.R. research*
Natural gasoline	88·8	25·2	79·1	76·5
Gasoline C	60·5	6·6	55·4	53·5
Blend of C and Natural	65·5	11·7	60·7	61·5

Investigations made for the Natural Gasoline Association of America [3, 4] developed many relationships between volatility of motor fuels and their performance in motor-cars, which were summarized as follows in 1930:

'The ease with which a motor will start, the length of time required to warm it up, and the character of its general performance are almost wholly dependent upon the volatility of the fuel as indicated by the A.S.T.M. distillation curve. The 10-per cent point is related to the lowest engine temperature at which satisfactory starting may be obtained and the lowest mixture temperature at which the car may be operated. The 35-per cent point is related to the lowest mixture temperature at which satisfactory performance may be obtained during the warming-up period and therefore determines the length of time necessary to warm up the motor. The 65-per cent point is related to the lowest mixture temperature at which perfect performance can be obtained. For these reasons the 10-, 35- and 65-per cent points should be low to insure satisfactory starting, warming-up, and general performance. The 90-per cent point, however, should not be so low as to indicate a dry mixture, for this means loss in power or acceleration with many modern cars equipped with heated manifolds and accelerating devices. The vapour pressure of the fuel or the 10-per cent point should not be so low as to indicate trouble from vapour-lock.

'The relations developed in this Bulletin make it possible to determine the volatility characteristic of a fuel for any desired engine performance.'

The general relationship between ease of starting a motor and the 10% point on the A.S.T.M. curve is, as expected, that the more volatile gasoline which has a lower 10% point will start at lower engine temperatures. Within the limits of ordinary motor fuel satisfactory starting should be obtained if the 10% evaporated point is less than or equal to the expression: 1·2 (100+engine temperature in ° F.). If the motor will start satisfactorily, it may be kept running by the proper use of the choke.

Shortly after starting the motor, or in the warming-up period, it is desirable to discontinue the use of the choke and still have satisfactory performance. The volatility of the fuel which will ensure satisfactory performance under these conditions is related to the middle part of the A.S.T.M. curve as represented by the 50% point.

Choke may be dispensed with when the mixture temperature reaches about one-half the temperature in ° F. of the 50% point. Ordinarily satisfactory performance may be obtained without use of the choke within a few moments after starting, the actual delay depending on the warming-up characteristics of the car, if 50% A.S.T.M. temperature in ° F. = 160+atmospheric temperature.

If the choke is to be used at a fixed setting during the warming-up period, fairly satisfactory operation may be obtained when the 35% point on the A.S.T.M. distillation is less than 100+1·3 mixture temperature ° F., which corresponds approximately to 190+atmospheric temperature °F.

The best operation of a motor with accelerating well and heated manifolds under steady driving conditions is obtained by having approximately 70% of gasoline vaporized in the mixture in the manifold. This requirement may be stated in terms of volatility as follows: A mixture temperature in ° F. approximately equal to one-half the 70% evaporated temperature on the A.S.T.M. distillation will give perfect performance in most cases. Also, if complete vaporization is undesirable, as when using heated manifolds and accelerating devices, the 90% point cannot be too low. It should be high enough to ensure the presence of liquid, but low enough to give complete combustion in cool motors.

Later work on the effect of using more volatile fuels [6, 1936] allowing the use of lower mixture temperatures indicated increases in power comparable with increases in power obtained by increases in octane number. A lowering of the mixture temperature of 50° F. made possible by using more volatile fuels gave an increased power equivalent to an increase in octane number of 25 units, provided proper motor adjustments are made in both cases. The realization of the above advantages and the increased production of vapour-recovery gasoline at refineries has caused a definite trend of increasing volatility of motor fuels in the United States.

The blending of natural gasoline with refinery straight-run or cracked gasoline provides the more volatile fuels which have the superior properties. The blending of a natural gasoline and a refinery product to make a motor fuel of specified volatility is easily predicted. If complete separation of the various boiling-point hydrocarbons were obtained by the A.S.T.M. distillation, the percentage evaporated at any temperature for the blend would simply be the percentage evaporated for component *A* times the fraction of *A* in the blend plus the percentage evaporated of component *B* times its fraction in the blend. However, due to inefficient fractionation by the distillation, particularly at temperatures below about 210° F., it is necessary to apply a correction as shown in Fig. 5 to the percentage evaporated when calculated in this manner [4]. For example, if a blend is to be made of the natural and refinery gasolines shown in Fig. 4 using 25% by volume of natural gasoline and 75% of refinery, the A.S.T.M. of the curve may be found as follows: At 120° F. the percentage evaporated on blend will be $0{\cdot}25 \times 67 + 0{\cdot}75 \times 2{\cdot}5 = 18{\cdot}5\%$, which corrects to 13% evaporated for the blend at 120° F. Likewise, at 200° F. the percentage evaporated on the blend will be $0{\cdot}25 \times 91{\cdot}5 + 0{\cdot}75 \times 28{\cdot}8 = 44{\cdot}5$, which corrects to 42% for the blend. Thus the experimental curve of the blend shown by the figure may be calculated with an accuracy approaching experimental in many cases. The calculation does not include the first and final portions of the curve, but it has been shown that the 10% and 90% points are sufficiently accurate for predicting terminal properties.

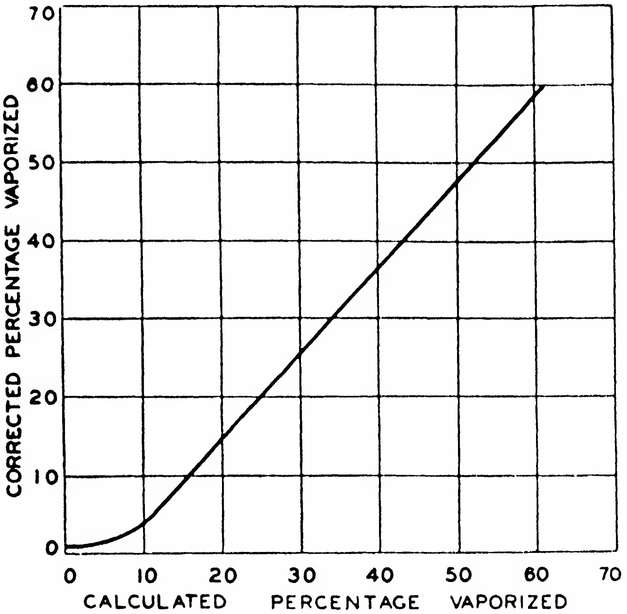


FIG. 5. Correction chart for calculated % evaporated on A.S.T.M. curve of blends.

In referring to gasolines of varying degrees of volatility, it is highly desirable to have a single number by which the volatility could be identified. Oberfell and Alden [17, 1933] have suggested such a measure of the volatility of motor fuels in their *Volatility Index*. They define *Volatility Index* as 284°—° F. of 50% point on A.S.T.M. distillation curve. The 284° F. was chosen because it is the specified maximum 50% point on U.S. motor gasoline which was arbitrarily given a volatility index of zero, as less volatile fuels are seldom marketed. A fuel having a 50% point at 219° F. as shown in Fig. 4 would have a volatility index of 284−219 = 65. This use of a single number to indicate volatility is advantageous and is found to indicate rather clearly the volatility of the gasolines which are made by refinery and blending practices as parallel as those of the majority of manufacturers in the United States.

In making blends it is necessary to consider vapour pressure and octane number along with the volatility.

The *Vapour Pressure* specifications of motor fuels are regulated to give gasolines which will not lose excessive amounts by evaporation in transit from refinery to the engine cylinder and which will not cause vaporization in the automobile fuel system to the extent that the fuel-handling system will not provide fuel for operation of the motor. The actual vapour pressures used for motor fuels vary from about 8 to 14 lb., depending upon atmospheric temperatures, altitude, and conditions. Refinery gasolines vary from a low figure of about 3-lb. vapour pressure up to the 8–14 lb. used as motor fuel. Low vapour-pressure products may be raised to the above vapour pressures by blending with natural gasolines or with vapour-recovery gasoline.

The effect of high vapour-pressure gasolines on vapour locking in the automobile fuel system has been frequently discussed [5, 1934], and the automobile manufacturers are studying the problem of allowing more volatile fuels without vapour lock. Present recommendations are that the Reid vapour pressure, A.S.T.M. method D. 417–35T, of fuels as delivered to the fuel tank of the vehicle for use at a maximum atmospheric temperature of 100° F. should not exceed 8 lb.; at a maximum atmospheric temperature of 85° F. should not exceed 10 lb.; and at a maximum atmospheric temperature of 75° F. should not exceed 12 lb. [5, 1934]. The improvement in fractionation in gasoline plants to eliminate propane and iso-butane from gasoline has allowed the use of more normal butane or of more natural gasoline in a blend. This step, along with improved design of fuel systems, has given value to butane which otherwise would have been wasted and now can be included in greater concentrations in motor fuel without causing vapour lock.

The A.S.T.M. method D. 417–35T of obtaining vapour pressure, known as the Reid method, determines the vapour pressure at 100° F. when the vapour space is equal to 4 times that of the liquid. In cases where only small portions of all constituents present in measurable quantities are vaporized in the procedure, the Reid vapour pressure is comparable to the absolute air-free vapour pressure of the gasoline.

Absolute vapour pressures of gasolines at ordinary temperatures may be calculated by Raoult's law and the composition of the gasoline with a reasonable accuracy because of the low pressures encountered and no constituents are near their critical temperature. The sum of mol concentration times the vapour pressures of the pure constituents gives the vapour pressure of any mixture. For natural gasolines, low-temperature fractionations may be used to obtain the analyses through hexanes or heptanes with determination or arbitrary assignment of properties of the residue. For motor fuels or refinery products, the low-temperature analysis of butane and pentane present may be made and the remainder analysed by distillation. A knowledge of the analyses of two materials to be blended would allow the calculation of the percentages required to give any vapour-pressure product.

A relationship has been devised between the A.S.T.M. distillation of both motor fuels and natural gasolines and the percentage of the lighter hydrocarbons present; propane, butane, pentane, and hexane [2, 1933]. These relationships might be used to obtain the analyses of the two materials to be blended. The analysis of any percentage blend, then, could be calculated and the vapour pressure estimated from this analysis. However, the Reid vapour pressures of blended motor fuels may be most satisfactorily estimated by using the relationship of Trimble and Richardson [24, 1935] on the calculated A.S.T.M. curve of the blend. They related the 5% and 20% evaporated temperatures to the Reid vapour pressure as shown by Fig. 6. The vapour pressure of the blend of Fig. 4 and Table VI as given by this nomograph is 11·6 lb. as compared with the experimental Reid vapour pressure of 11·7 lb.

The *Octane Number* of motor fuels has gone through a transition of standards for testing, and it is somewhat difficult to correlate data over a period of time because of these differences. The present accepted method is the A.S.T.M. test D. 357–34T, using the Co-operative Fuel Research (C.F.R.) engine, and is similar to the C.F.R. motor method. The C.F.R. research method differed from this method in various details such as speed of motor. The octane numbers of some pure hydrocarbons [15, 1934] present in natural gasoline are given in Table VI using the A.S.T.M. D. 357–33T method. In general the A.S.T.M. method of obtaining octane number on natural gasolines gives higher values [23, 1933] than the C.F.R. research method, although the opposite is true for many motor fuels. The volatile hydrocarbons which are objectionable from a vapour-pressure standpoint have high octane numbers. This is especially true for the isomeric compounds. Therefore, natural gasolines would be expected to have high octane numbers and materially raise the octane number of refinery straight-run gasolines upon blending.

A relationship between octane number and Reid vapour pressures was presented by Alden [1, 1932]. His data are shown graphically by Fig. 7. The octane numbers presented are by the C.F.R. research method and would in general be slightly lower than the A.S.T.M. D. 357–34T method. The higher vapour-pressure gasolines have the higher octane number because of the high concentrations of butanes present. Twenty-six-pound gasolines have octane numbers of 77–8, while 12-lb. gasolines have octane numbers of 66–8.

The resultant octane number when blending a natural gasoline with a refinery product is of equal importance to its original octane number. Also the effect of the tetra-ethyl lead (T.E.L.) requirement to bring a fuel up to some standard number, such as 70 or 76, is of importance when using natural gasoline blends. If straight-line relations held when blending two materials of known octane number, it would be a simple matter to multiply the percentage of each component by its octane number and add the numbers to give the octane number of the blend. This method gives an approximation which might be fairly good, as in the case of the blend represented by Table VI and Fig. 4. The octane number of the natural gasoline is given as 79·1 by the A.S.T.M. method and 76·5 by the C.F.R. research method. Fig. 7 would give a C.F.R. research number of 77 based on the Reid vapour pressure. The base refinery fuel has an A.S.T.M. octane number of 55·4. The sum of $0{\cdot}25\times79{\cdot}1$ and $0{\cdot}75\times55{\cdot}4 = 61{\cdot}3$ calculated number as compared to an experimental number of 60·7. However, if the analyses of natural gasolines and the octane numbers of the pure components are used in a similar manner, a resultant octane number about 15% too low may be calculated even if liberal quantities of isomeric compounds are considered to be present in the hexanes or heptanes and heavier fraction. Therefore, it is necessary to rely on experimental data to obtain reasonable accuracy when predicting the octane number of blends.

The lead response is defined as the increase in octane number obtained by adding a given quantity of tetra-ethyl lead (T.E.L.) such as 1·0 c.c. to one U.S. gallon of gasoline. The major portion of the U.S. motor fuels sold are

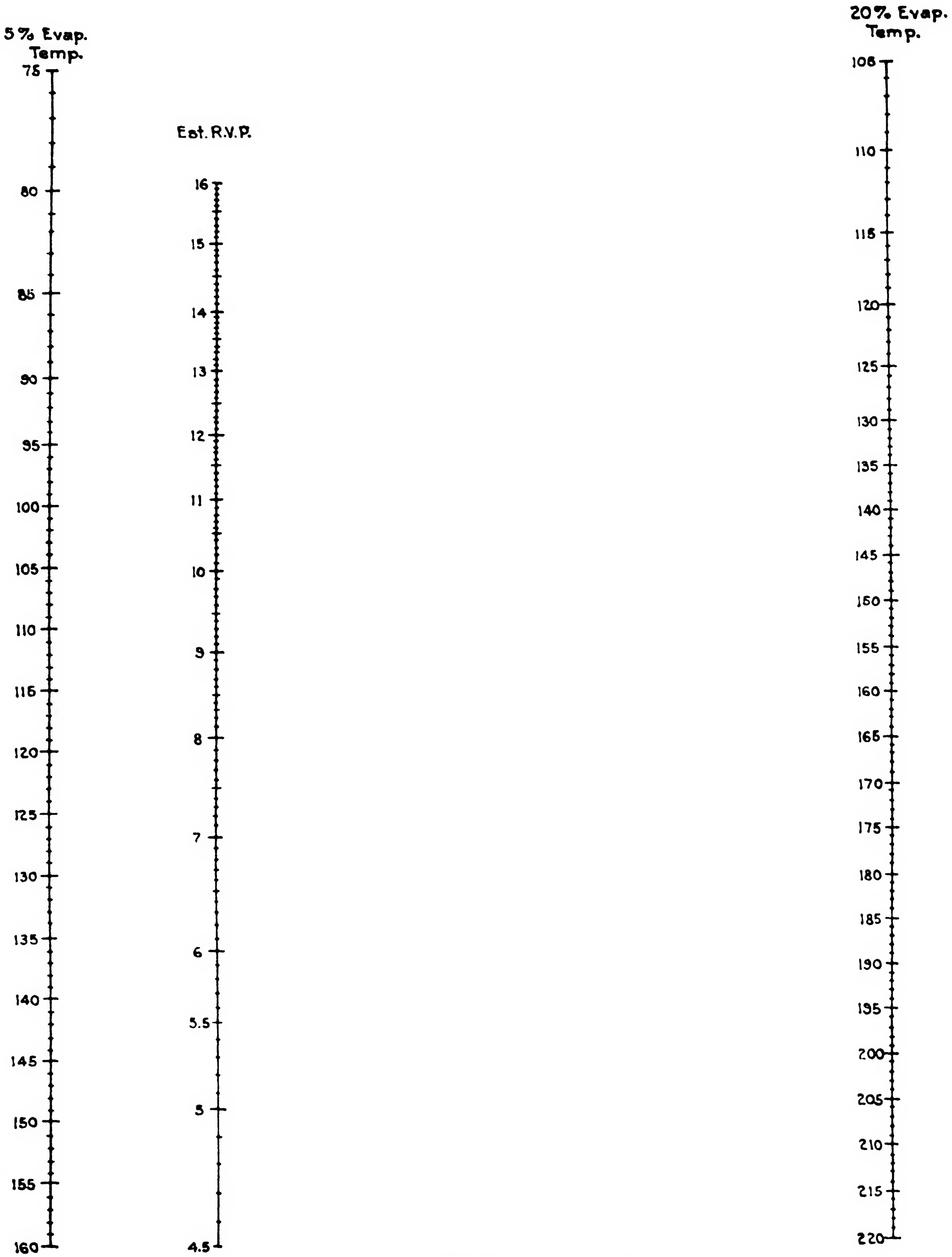


FIG. 6. Relationship between A.S.T.M. distillation and Reid vapour pressure.

raised to the marketed octane numbers of 70 or 76 by use of tetra-ethyl lead. Therefore, the effect of blending natural gasoline with refinery products on the lead response of the blend is important. In general, the lead response of natural gasoline blends is considerably superior to that of the base stock. The lead response of natural gasolines themselves is shown by Alden [1, 1932] to be equal to or better than the refinery straight-run gasolines and superior to cracked gasolines. A fraction composed of the high-boiling portion of natural gasoline showed a low lead response.

A composite effect of blending value and lead response when blending natural gasoline and its constituents with refinery gasolines was presented by Neptune and Trimble [15, 1934]. Figs. 8, 9, 10, and 11 show the effect of iso-butane, normal butane, iso-pentane, and normal pentane on tetra-ethyl lead requirements of various percentage blends as compared to the T.E.L. requirement of the base stock for an equal octane number. The higher volatility compounds show a greater reduction in T.E.L. requirements in line with their higher octane numbers. The total reduction in tetra-ethyl lead required to obtain any given octane number gasoline cannot be attributed to the increase in octane number of the unethylized blend alone, but to the increased lead response of the blend. Therefore, natural gasolines composed of these compounds would be expected not only to raise the octane number of the blend in proportion to its concentration, but to lower the T.E.L. requirement of the blend to make a definite octane gasoline more than predicted by the increase in octane number of the blend.

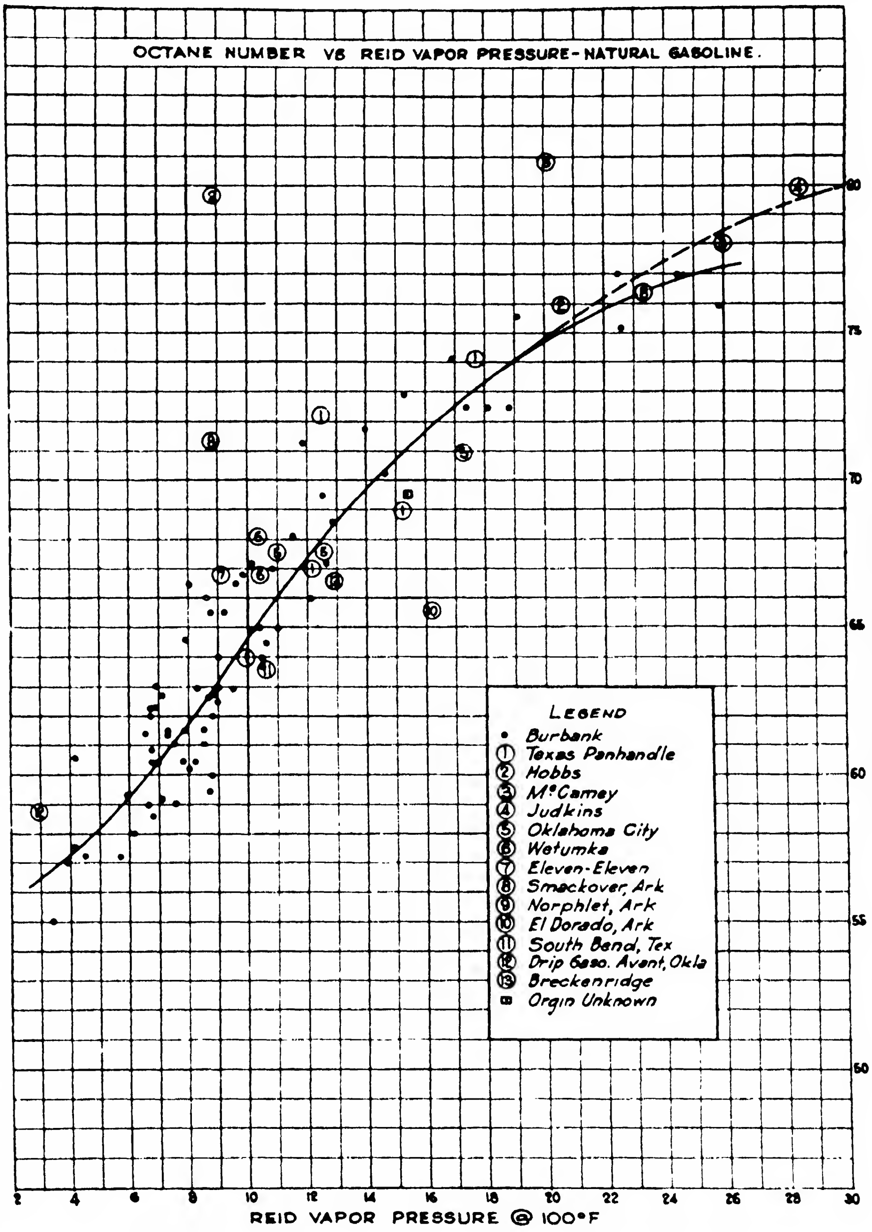


FIG. 7. Octane number *v*. Reid vapour pressure for natural gasolines.

The composite effect of the blending of natural gasolines on the tetra-ethyl lead requirement to make a specified octane number gasoline is shown as a function of T.E.L. requirement of base stock, the percentage of natural gasoline added, and the vapour pressure of the gasoline by Fig. 12 [15, 1934]. The chart may be used as follows: A base stock of refinery and straight-run gasoline requires 2·0 c.c. of tetra-ethyl lead per U.S. gallon to raise it to some octane number such as 76. If 14% of a 14-lb. vapour-pressure gasoline could be blended to 60% of the stock and give the required volatility and vapour pressure, the resultant blend would require only 1·0 c.c. of tetra-ethyl lead to bring it to the 76 octane number.

Blending of natural gasoline with refinery products has been shown to have effects on the volatility, vapour pressure, and octane number of the blends. Improvements in the quality of motor fuels by blending with natural gasolines are always obtained when considering the fuel from volatility or detonating characteristics. The proportion of natural gasoline which can be blended with refinery products is definitely limited by the increase in vapour pressure caused by the natural gasoline. Unblended natural gasoline when reduced to 12 or 14 lb. vapour pressure has qualities which make it a desirable motor fuel for low atmospheric temperatures.

The *special products* made from natural gasoline include aviation gasolines as well as special fuels and solvents. Aviation gasolines are characterized by their low vapour pressure, high volatility, and high octane number requirements. Natural gasolines fulfil the octane number and volatility requirements exceptionally well, but are under a handicap with respect to vapour-pressure specifications. However, many aviation gasolines have been made by blend of natural gasoline and other products. Such practices as fractionating out the normal paraffin hydrocarbons which have a low octane number and combining the isomeric compounds of natural gasoline to give an extraordinarily high octane natural petroleum mixture have been successfully tried. Iso-pentane, because of its ease of manufacture and high octane number of 90, is a valuable blending agent with synthetic iso-octanes manufactured for aviation fuels [16, 1936].

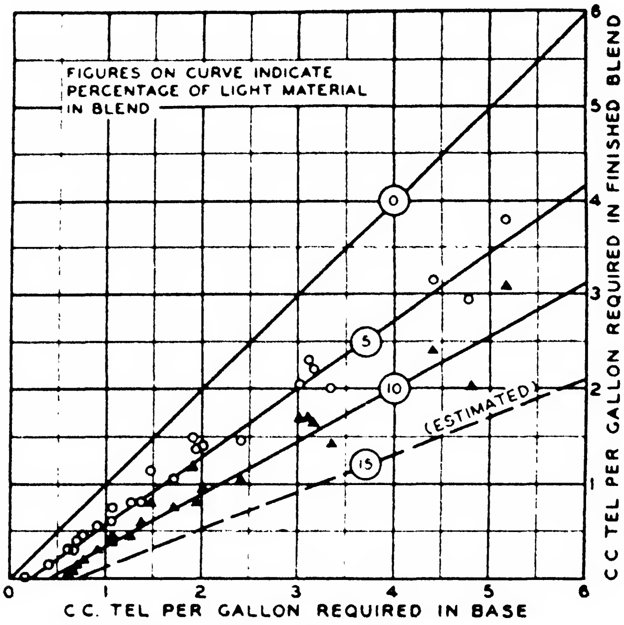


FIG. 8. Effect of iso-butane on T.E.L. requirements.

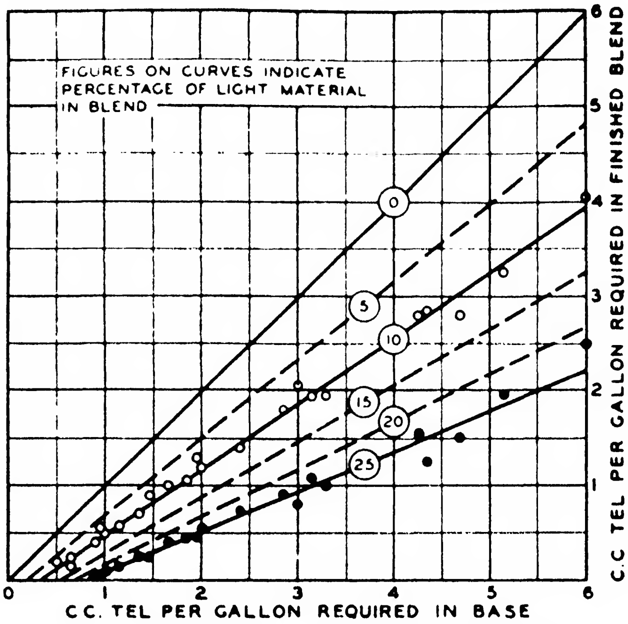


FIG. 10. Effect of iso-pentane on T.E.L. requirements.

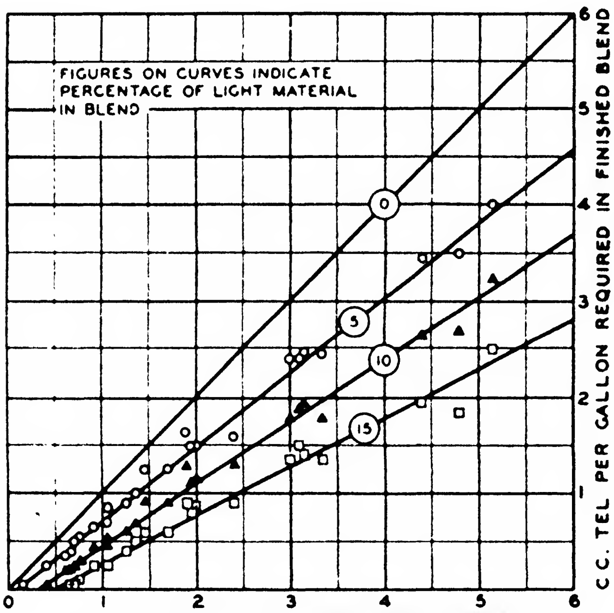


FIG. 9. Effect of normal butane on T.E.L. requirements.

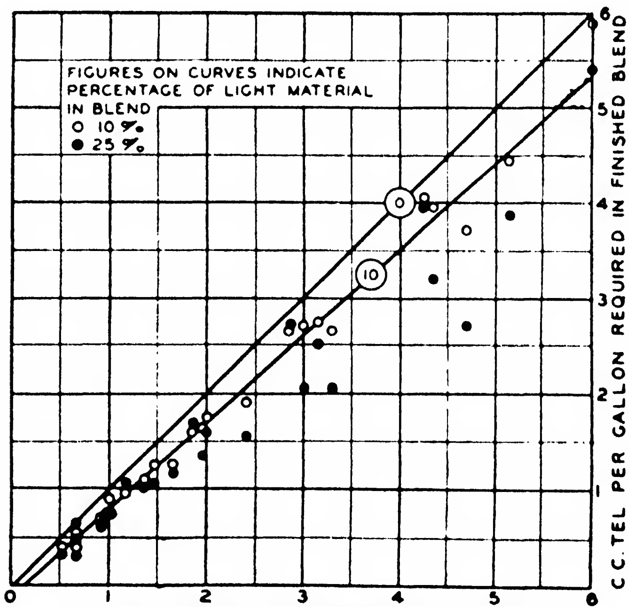


FIG. 11. Effect of *n*-pentane on T.E.L. requirements.

Solvents for various purposes are made by fractionating natural gasoline into various boiling-point fractions. The removal of paraffin from oil-wells and pumping equipment is accomplished by natural gasoline or various fractions. Solvents for the paint and varnish industry may be made from natural gasoline. The absence of unsaturated gum-forming hydrocarbons which are present in cracked products and the relatively high concentration of low-boiling fractions in natural gasoline facilitates solvent production from this source.

The liquefied petroleum gas (L.P.G.) industry is an industry which utilizes the otherwise waste products of the natural gasoline industry. Liquefied propane and butane are distributed for domestic and high-grade industrial heating. This propane and butane is obtained in the extraction of the natural gasoline because of its presence in the natural gas and is in excess of the allowable butane used in motor fuels. The Liquefied Petroleum Gas industry is described in detail elsewhere in this series of articles.

Raw natural gasoline recovered from natural gas which was separated from crude oil under high pressures may contain large proportions of high-boiling compounds which are undesirable in gasoline. In those cases it is necessary to separate the extracted gasoline into a heavy fraction and natural gasoline. The heavy fraction has been used as a blending agent for Diesel fuels and would have the properties of a light straight-run gas oil or distillate.

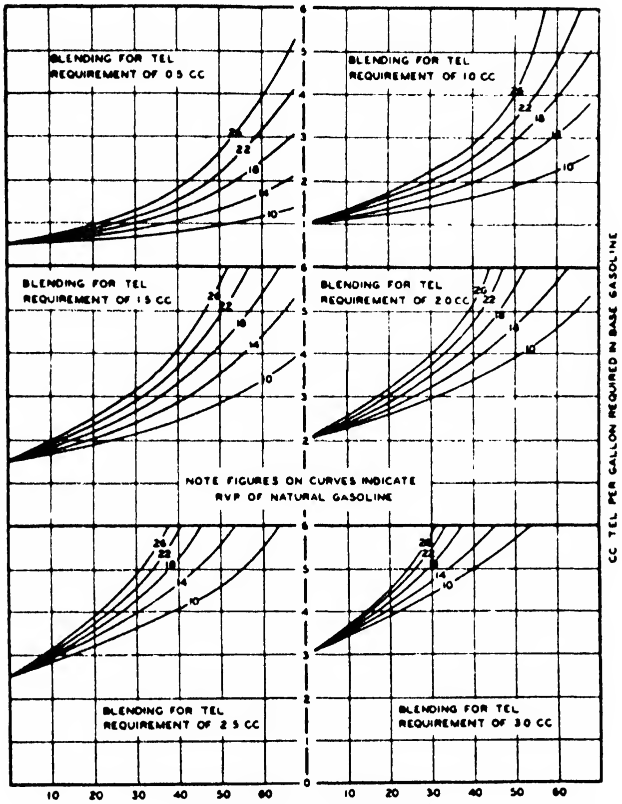


FIG. 12. Chart for blending to lower T.E.L. requirements by using various percentages of the several vapour-pressure natural gasolines.

The major development in the by-products of the natural gasoline industry is the recovery of butane and propane for feed stock to the new polymerization processes. As mentioned previously, natural gasoline plants designed to recover substantially all the pentanes will extract large quantities of butane and propane. The butane extracted is normally in excess of that required to make 26-lb. natural gasoline, and so waste butane is available in varying quantities depending on the vapour pressure of gasoline made. The high concentrations of propane and butane normally present in natural gas may be more completely recovered by simple changes in gasoline extraction plants. The new polymerization or cracking processes which convert butane, propane, or ethane into motor fuel are beginning to place a value on a formerly waste product. The recovery of the butane and propane for feed stock is in the realm of the natural gasoline industry and is a commercial operation at the present time. The quantity of motor fuel produced using natural gas butane and propane may surpass the natural gasoline production at some future date. The development of polymerization processes make natural gas reserves potential sources of complete high-quality motor fuels.

Summary

The recovery of natural gasoline from natural gas has converted a waste or low-grade product into a high-class fuel such as motor fuel. The industry increases the lifetime of petroleum production and increases the motor-fuel reserves even from known supplies of hydrocarbons. The chemical and physical properties of natural gasoline are rather well known because of the relatively high concentrations of known compounds present in the gasoline. This knowledge has caused the scientific development of extraction processes, methods of manufacture, and utilization to a rather high degree. Natural gasoline finds its primary use as a blending agent in making high-quality motor fuel, but the industry has developed many important auxiliary products.

REFERENCES

1. ALDEN, R. C. *Nat. Petr. News*, **24**, 32 (20 Jan. 1932).
2. BLAIR, M. G., and ALDEN, R. C. *Ind. Eng. Chem.* **25**, 559 (1933).
3. BROWN, G. G. *The Relation of Motor Fuel Characteristics to Engine Performance.* University of Michigan Engineering Research Bulletin no. 7, Ann Arbor, Mich.
4. —— *The Volatility of Motor Fuels.* University of Michigan Engineering Research Bulletin no. 14, Ann Arbor, Mich.
5. —— *Motor Fuels and Vapor Lock.* A.S.T.M. preprint 78 (1934).
6. —— *Oil and Gas J.* **34**, 16 (16 Jan. 1936), and 28 (23 Jan. 1936).
7. BROWN, G. G., SOUDERS, MOTT, SMITH, R. L., SELHEIMER, C. W., and HYLAND, H. V. *Ind. Eng. Chem.* **24**, 513 (1932).
8. BURRELL, G. A. *The Recovery of Gasoline from Natural Gas*, 33 (Chemical Catalog Co., 1925).
9. California Natural Gasoline Association.
10. GREGORY, L. S. *Oil and Gas J.* **33**, no. 14, 45 (1935).
11. KATZ, D. L. *Oil Weekly*, **75**, 19 (Oct. 1934).
12. —— *Trans. Amer. Inst. Min. Met. Engrs.* (*Petr. Dev. Tech.*) **118**, 18 (1936) .
13. LINDSLY, B. E. *Petr. Eng.* **7**, 34 (Feb. 1936).
14. Natural Gasoline Association of America, Tulsa, Oklahoma.
15. NEPTUNE, F. B., and TRIMBLE, H. M. *Oil and Gas J.* **32**, **44** (10 May 1934).
16. NEPTUNE, F. B., TRIMBLE, H. M., and ALDEN, R. C. *Nat. Petr. News*, **28**, 25 (6 May 1936).
17. OBERFELL, G. G., and ALDEN, R. C. *Oil and Gas J.* **31**, 14 (19 Jan. 1933).
18. ———— *Natural Gasoline* (1924). (Book.)
19. Private communication, Phillips Petroleum Company.
20. SAGE, B. H., and LACEY, W. N. *Oil Weekly*, **79**, 31 (18 Nov. 1935).
21. SAGE, B. H., LACEY, W. N., and SCHAAFSMA, J. G. *Ind. Eng. Chem.* **26**, 214 (1934).
22. STARMONT, D. H. *Oil and Gas J.* **34**, 244 (14 May 1936).
23. TRIMBLE, H. M. *Oil and Gas J.* **31**, 58 (18 May 1933).
24. TRIMBLE, H. M., and RICHARDSON, J. O. *Refiner*, **14**, no. 12, 562 (1935).
25. WESTCOTT, H. P. *Handbook of Casinghead Gas*, 13 (1922). Metric Metal Works, Erie, Pa.

AVIATION FUELS

By RAYMOND HASKELL, Ph.D.

The Texas Co., New York

UNTIL the latter part of the World War there was no definite call for a special gasoline for aviation purposes. Regular government or navy gasoline, up to as late as 1913, was almost as volatile as the most volatile type in 1935; in fact, in 1910 it was more volatile than Fighting Grade in 1935. About this time (1917), however, the demand for gasoline became so great, due to automobile production, that there was a fear of shortage. This apparent shortage was met by increasing the range in the higher boiling fraction and thus decreasing the average volatility. Cracking of fuel to make more gasoline had not at that time reached the prominence that it later acquired.

At the same time improved design in airplane engines permitted increased efficiency and greater power. To get this power, however, a more volatile gasoline was necessary than requisite for automobile equipment. The United States navy recognized this in 1918 and issued a specification for aviation gasoline which called for an increased volatility over regular gasoline. This increase was brought about by lowering the average boiling-point, though the initial and 10% points were not changed. About a year later the above specification was replaced by two specifications, both more volatile than automobile gasoline. These two specifications were called:

(1) Fighting Grade.
(2) Domestic Grade.

The chief difference between these two grades pertained to volatility, the Fighting Grade having the lower 90% point. These two specifications are still the standards of the government and industry, practically as issued, though the volume of Domestic Grade used is decreasing in comparison to the volume of the Fighting Grade. The more recent changes made in these specifications relate particularly to the Fighting Grade. Addition of tests to meet a requirement for better anti-detonating qualities have been added and an increase in stability under severe operating conditions is now required.

General Requirements.

The most important characteristics which aviation gasoline must possess are correct volatility, high anti-knock value, and excellent stability.

Volatility. The degree of volatility required is, in the final analysis, a function of engine design, as well as the operating conditions under which the engine must perform satisfactorily. Nevertheless, there are certain fundamentals that exist, almost regardless of the design of the power-plant, though these may not apply where solid injection is used as a means of distribution of fuel.

A. The greater the volatility, the better the distribution to the cylinders. This results in more uniform and efficient firing, provided, of course, that carburettion is uniform under different operating conditions, particularly as relating to loads, speeds, and altitude.

B. High volatility favourably influences ease of starting and decreases the length of time necessary for thorough warming up. It also allows quick response to the throttle under cold conditions, provided icing is prevented.

C. Too high a volatility may cause icing where air temperatures approach the frost-point unless the system is particularly designed to handle this condition.

D. Too high a volatility, especially as regards the fractions that boil at the lower temperature, may cause vapour lock.

E. Too high a vapour pressure may not only cause vapour lock but also may indicate that there will be a loss of fuel from the airplane fuel-tanks at high altitudes, especially when there is a big difference in temperature between the ground- and cruising-levels.

The rate of evaporation from fuel-tank depends on actual vapour pressure at the temperature of the evaporating surface, as well as upon the atmospheric pressure. The lower the temperature of the gasoline, the less the evaporation, and losses may become serious only in cases of high upper air temperature or where the climb is so rapid that the temperature of the fuel cannot equalize itself to the temperature of the air and hence lower its vapour pressure.

It will be seen, therefore, that volatility may be considered under two heads: (*a*) general; (*b*) low temperature, or initial. General volatility is desirable from the standpoint of distribution, warming up, and quick response to the throttle. Initial volatility is desirable in respect to starting, but not in regard to vapour lock and icing and possible loss at high altitudes.

Icing. Icing can be defined as the formation of ice within the carburettor or intake manifold due to the latent heat of gasoline. If this absorption of heat from the intake air reduces the air temperature below the ice- or snow-point under the humidity conditions existing, ice will form. The temperature attained may depend in some degree on the rate of evaporation. If all the gasoline does not evaporate in the carburettor but is carried along in a fog to some hotter point, icing will be decreased. In some cases this may not produce an even distribution to the cylinders and may even cause trouble in the blowers, so it is not particularly desirable, though not necessarily serious.

To prevent icing, therefore, it is safest to maintain the air-gas mixture out of the carburettor above 40° F., though this may not be necessary in very dry climates. Icing is usually prevented by heating the intake air, and often it is advisable to maintain a temperature of 150° F. If the temperature is too high—and sometimes 160° F. is too high—detonation may result with loss of power and overheating of the piston-head and cylinder. This is most apt to happen on take-off or climb and depends on the anti-knock value of the fuel. Devices are now available to regulate the heating of the intake air to meet the manifold temperature conditions desired.

Some success has been attained by the use of special alcohol mixtures on take-off until heating conditions are stabilized. The alcohol can be injected separately or mixed with a fuel especially designed for starting. It is claimed by some that less alcohol is necessary if used alone.

Vapour Lock. Vapour lock can be considered any uneven operation due to formation of gas or vapour in gasoline lines, pump, or carburettor beyond the capacity of the system to handle. Unless provision is made to remove this vaporized gasoline, an uneven metering results with resultant erratic firing and perhaps complete stoppage of the engine. The ability of an engine system to accommodate itself to this vapour formation is called its 'vapour-handling capacity'. The tendency of a gasoline to form vapour depends on the ratio of vapour volume to liquid volume (*V*/*L*) which will exist when that gasoline is heated to the definite temperature and pressure conditions under consideration. Roughly, this is a function of vapour pressure when the vapour-handling capacity of the engine is low. If this latter is high, the 10% point may be the controlling factor. Engine manufacturers try to keep their vapour-handling capacity high, and fuel refiners endeavour to keep the vapour pressure low.

Solid Injection. As stated above, carburettor icing is a real difficulty, especially when high octane is produced by the use of a gasoline containing a very large percentage of low-boiling fraction. Icing can be prevented if fuel is injected directly into the hot cylinder or adjacent manifold section. Some success has been attained by this type of intake system, but it is still somewhat incompletely developed as to simplicity, flexibility, and general operating efficiency. No doubt this system will shortly be made practical and reliable and thus increase the number of types of motive-power producers available.

Detonation. In view of the improvements in the gasoline handling system of airplane engines, volatility control is becoming of less importance than the anti-detonation qualities of the fuel. Engines are becoming more and more efficient due to improved design, regardless of the type of gasoline used, but the greatest strides can be made only if the mean effective pressure and expansion ratio is increased. Such increase results in higher fuel-mixture temperatures on compression, which in turn increases the tendency to detonate, especially where full-power operation is demanded. This, of course, influences operation on take-off or high-speed operation at low altitudes, as is the case with military manœuvres. The availability of higher power per weight of power-plant or its corollary, the increase of cruising per unit of weight carried, is, of course, of paramount interest to the military branch of government. The commercial airline operators are also interested in high mean effective pressures because they mean increased efficiency in operation, provided such efficiency does not necessitate a more than compensating increase in cost.

The use of detonation retarders, as tetra-ethyl lead, to increase anti-detonating qualities, has about reached its limit using regular aviation gasoline; hence, an increase in compression ratio, or supercharging resulting in higher mean effective pressures, is dependent upon the synthetic production of a higher anti-knock gasoline. The same results can be obtained by the use of the Diesel cycle. Both systems are being highly developed, and improved design will probably make them both available in a few years. They are both striving for the same objective, namely, low specific fuel consumption and low weight per horse-power developed. In the matter of weight, not only must the power-plant be considered, but also the weight of the fuel necessary to generate the power.

100 Octane Fuel.

Synthetic fuels of higher detonation characteristics have been produced and can be made in commercial quantities as the raw materials are available. At the present time it is a question of relative cost; that is, will the cost of fuel, plus the increased cost of engine to use this synthetic fuel, be greater than the increased revenues brought about by its use? Experimental figures say No. Already, with a special engine an increase of efficiency of 30% has been attained, and at least half of this figure can be reached with very little change in design. This saving in efficiency, if put into dollars saved or earned by allowing an increase in pay-load, will more than compensate for even a large increase in unit fuel cost. How large this increase in cost will be will depend upon the quantity of fuel demanded.

Up to the present time there is no way of making a proper synthetic fuel in a single continuous operation. In other words, high anti-knock and proper volatility cannot be obtained from a single source of raw material. Therefore, a blend of several synthetic fuels must be made. Solid injection may alter this situation somewhat, though in any case there must be sufficient low-temperature volatility to start in cold weather.

As stated above, engine design is changing to meet the necessity of keeping cylinders cool under high-load conditions, and it is believed engines capable of utilizing the potential value of high anti-knock fuels are practically very near. Specifically, a fuel efficiency in practice of 0·35 lb. of fuel per brake horse-power is not a remote possibility. Experimental engines showing over 400 lb. mean effective pressure have already been developed.

Diesel Engine.

At this point mention should be made of the rapid development of the Diesel engine for aircraft purposes. The problem here is not so much one of fuel efficiency, as fuel economy of 0·35 lb. per brake horse-power is attainable, but one of simplicity of design and flexibility in operation. Advantage is claimed in regard to fire hazard, though this is disputed by some, since often it is a question of spontaneous ignition and not spark ignition; and there is evidence that the fire may originate with the lubricating oil. Some advantage is also claimed in radio operation, due to elimination of spark.

Many large airplanes, as well as airships, are equipped with Diesel engines and apparently are working satisfactorily, and as soon as the weight per horse-power of total power-plant can be made as low as the gasoline engine, with equal ease of operation, competition will truly exist.

Stability.

Under this heading may be included not only those characteristics which govern the maintenance of properties in storage, but also those which cause or allow the gasoline to give its maximum efficiency under diverse operating conditions.

Gum formation in storage or in the engine prior to actual burning was at one time a serious proposition, but a partial knowledge of its causes has allowed refiners to establish certain restrictions in the form of required tests that mitigate the evils to a large extent. In fact, there is considerable belief that some tests—such as the Accelerated Oxidation Bomb Test—are too severe and may throw out some gasolines that are perfectly satisfactory in engines. This will probably be corrected as knowledge increases. Inhibitors will undoubtedly assist. At one time there were many examples of corrosion due to improperly treated gasoline. These cases at present are practically nil. However, there is still some complaint that metals have not yet been developed which will withstand, under all conditions, the erosive or corrosive effects of certain substances added to improve burning qualities. This, no doubt, will be cured by co-operative efforts between the engine manufacturers and the oil-refiners.

In this same category belongs the use of alcohol, either as a knock deterrent, an anti-icing aid, or just a political requirement. Alcohol under some conditions may be strongly corrosive on burning and, if used in large proportional quantities, will reduce the life as well as the power of the engine.

Under this heading of 'Stability' can be discussed the falling-off of anti-knock power under high heat conditions. This is particularly noticeable with some types of cracked gasoline, and the present method of handling the situation is to bar them from use. No doubt some one will shortly find a way of correcting the difficulty, as it is poor economics not to allow the use of such a large potential source of high anti-knock gasoline.

Gravity.

Specific gravity, while once a factor in aviation fuel specifications, has almost ceased to be of value and is generally omitted. If, however, synthetic fuels become more generally used, gravity combined with available heat unit may again become of interest. In other words, the amount of useful heat per pound is of paramount interest and the amount of heat per gallon of less interest, though volume considerations may enter where long flights are involved.

In this connexion it must be remembered that the most economic air-fuel ratio must be considered both in regard to maximum power and maximum efficiency. In other words, the real criterion of power is the available heat per unit of volume of combustible mixture that enters the cylinder. The most economic fuel from a weight standpoint may not always give the maximum power for the engine.

Specifications.

Below are tabulated (see attached) the latest specifications of the U.S. Army and U.S. Navy, and commercial operators follow, in general, these specifications, though they may depart in minor respects.

The methods of test employed are described in detail in the specifications themselves. Those methods varying appreciably from the A.S.T.M. procedure, or not included therein, are briefly described below:

Water Tolerance. 80 ml. of the fuel are shaken in a glass-stoppered graduated cylinder with 20 ml. of distilled water at room temperature. On settling, the volume of aqueous layer shall not have increased or decreased by more than 2 ml.

Acid Heat. 150 ml. of fuel are placed in a 1-pint 'thermos'-type flask, the temperature recorded, and 30 ml. of commercial 66° Bé. sulphuric acid added. After shaking for total of 3 min. under specified conditions, the rise in temperature is recorded as the 'acid heat'.

Accelerated Gum. The fuel (200 ml.) is subjected to an accelerated ageing test at 100° C. with oxygen at approximately 100 lb. pressure for 4 hours, using the conventional bomb apparatus. 100 ml. of a mixture of oxidized sample and gum solvent are evaporated down, when the amount of residue shall not exceed 10 mg.

Copper Dish Corrosion. 100 ml. of the fuel are evaporated in a polished copper dish and should cause no grey or black corrosion.

Freezing-point. The freezing-point, as indicated by the initial formation of solid rather than by the cloud-point, shall not be higher than minus 60° C. (minus 76° F.).

Note: For a more complete list of former specifications, see Nash and Howes, ii. 409.

	U.S. Army				*U.S. Navy*					
Grade	*Domestic*	*Fighting*	*Fighting*	*Fighting*						
Designation	*2-93*	*2-95*	*2-90*	*2-92*	*M 222*				*M 302*	
Octane number	65 (*a*)	92 (*a*)	92 (*a*)	100 (*a*)	73	80 (*b*)	83 (*b*)	87 (*b*)	87 (*b*)	100 (*a*)
Lead tetra-ethyl (max.)	..	6 c.c.	0	3 c.c.	0	1·63 c.c.	2·29 c.c.	3·27 c.c.	0·5 c.c.	3 c.c.
Colour	..	blue	..	blue	+25 Say.	blue			Lt. blue or white	blue
Vapour pressure (Reid, 100° F.) (max.)	7 lb.	7 lb.	7 lb.	7 lb.	7 lb.				7 lb.	
Sulphur (max.)	0·1%	0·1%	0·1%	0·1%	0·1%				0·1%	
Water tolerance (max.)	±2 c.c.	±2 c.c.	±2 c.c.	±2 c.c.	..				±2 c.c.	
Acid heat	..	..	..	..	20° F.				20° F.	
Accelerated gum (max.)	..	10 mg.	10 mg.	10 mg.	10 mg.				10 mg.	
Copper dish, corrosion	none	none	none	none	none				none	
Copper dish gum	3 mg.	..	..	..	..				..	
Distillation:	Evap.	Evap.	Evap.	Evap.	Recov.				Evap.	
10%	158° F.	167° F.	167° F.	167° F.	167° F.				167° F.	
50%	230° F.	212° F.	212° F.	212° F.	212° F.				212° F.	
90%	320° F.	275° F.	275° F.	275° F.	275° F.				275° F.	
Sum 10% and 50% points	307	307	307	307	..				307	
Residue	2%	2%	2%	2%	2%				2%	
Freezing-point	−76° F.	−76° F.	−76° F.	−76° F.	−76° F.				−76° F.	

(*a*) = octane number by Army method of determination.
(*b*) = C.F.R. motor method.

BRITISH PRACTICE IN REGARD TO AVIATION FUELS

By F. R. BANKS, O.B.E., F.R.Aë.S., M.I.A.E., M.Inst.P.T.

Ethyl Export Corporation

Introduction

British practice in regard to aviation fuels is almost entirely controlled by or dependent upon the requirements of the British Air Ministry, which is by far the largest customer of the aircraft industry, being responsible for the whole equipment of the Royal Air Force. In so far as civil aviation is concerned, the principal air-line operating company, Imperial Airways, follows Air Ministry practice. The smaller companies who operate internal services in Great Britain, use equipment the engines of which will normally run quite satisfactorily on the usual 'No. 1' grades of automobile spirits which are generally available. Otherwise, Air Ministry fuel specifications are adhered to.

So far as the formulation of the actual fuel specifications is concerned, the Air Ministry co-operate with the aviation engine manufacturers, the fuel suppliers, and the Institution of Petroleum Technologists (I.P.T.), the official body in Great Britain of the petroleum industry, before coming to a final decision regarding the desired fuel quality or qualities.

The Ministry usually adopts the various tests for spirits which are prescribed by the Institution of Petroleum Technologists which, in turn, receives a large measure of support from the various technical departments of the Air Ministry in order to carry out the necessary development work which must be done before formulating such test procedure.

The fuel requirements for the Air Ministry are issued in the form of specifications from the Directorate of Technical Development (D.T.D.). There are two current specifications for aircraft fuels, namely, D.T.D. 224 and D.T.D. 230. (Reproduced as Appendices A and B.) The first specification calls for an octane value of 77 and excludes the use of tetra-ethyl lead, while the second one demands an octane value of 87 and allows the use of tetra-ethyl lead up to a concentration of 4 ml. per imperial gallon. In both, the use of added aromatics is permitted, subject to the freezing-points of the finished fuels not being above those quoted in the specifications.

The knock ratings of both these fuels are ascertained by testing them in a C.F.R. engine under conditions laid down by the I.P.T. for testing aviation fuels. These conditions follow, with one exception, the C.F.R. Motor Method test, adopted tentatively by the American Society for Testing Materials (A.S.T.M.), the exception being that of the temperature of fuel/air mixture, which for the Motor Method is 300° F. (149° C.), and in the case of the Modified (Aviation) Motor Method of the I.P.T. is reduced to 260 °F. (126° C.).

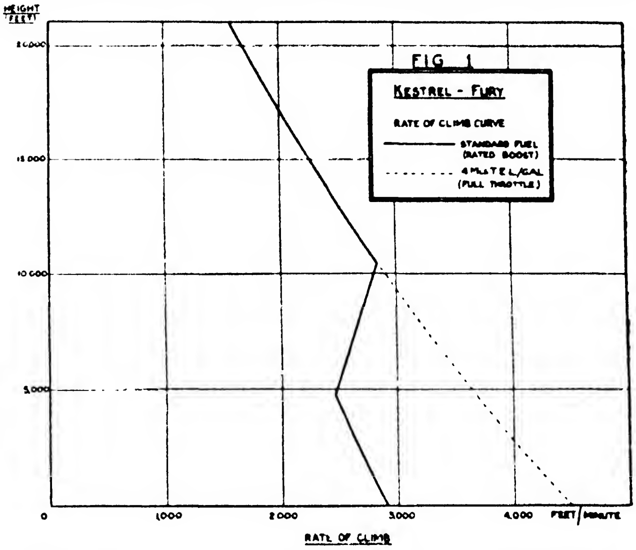
Conditions to be Considered and Satisfied in order to evolve a Satisfactory Aviation Fuel

There are a number of points which must be considered in order to produce a satisfactory fuel, and these are enumerated herewith, more or less according to their order of merit:

(*a*) Anti-knock Value.
(*b*) Distillation Characteristics.
(*c*) Vapour Pressure.
(*d*) Freezing-point.
(*e*) Freedom from Sulphur.
(*f*) Freedom from Gum.

(*a*) Anti-knock Value.

Anti-knock value is undoubtedly the most important point and one which governs the production of a suitable fuel, because it is upon this value that the performance and the reliability of the modern aviation engine so largely depend. Manufacturers are also taking more and more advantage of the improvement in anti-knock value to produce engines of still greater performance. This fact is equally true of military and civil aviation and where the case of the higher powered engine is particularly concerned.



(*Reproduced from paper entitled 'Ethyl', by F. R. Banks, 'Journ. Royal Aëronautical Soc.', April 1934.*)

All other things being equal, the anti-knock value of the fuel controls the power output of an engine by limiting the degree of compression ratio and supercharge which can be employed without encountering detonation and overheating troubles. There are many publications which deal with these questions at length, and reference is made to them at the end of this contribution [3, 1934]; [12, 1933]; [2, 1934].

A graphical illustration of the influence of anti-knock value as it affects the performance of an aeroplane may be of some interest, and in Fig. 1 two curves are reproduced which show the performance of a well-known aircraft under climbing conditions, with two fuels having widely differing anti-knock value. The full line represents the standard performance of the machine when using fuel (*a*) conforming to the Air Ministry's D.T.D. 134 specification, which has since been superseded. The anti-knock value was in the neighbourhood of 73 octane C.F.R. Motor Method. To avoid detonation with this fuel the throttle could only be opened, by a limited amount, to a 'gate' or stop until a height of about 4,500 ft. was reached, after which it was progressively opened beyond the 'gate' as the height increased. The amount of the throttle opening past this point during the climb is governed by a predetermined degree of supercharge or 'boost', indicated on a 'boost' gauge. Upon reaching the supercharged height, in this case about 10,500 ft., the throttle could be fully opened, and from this point to greater heights the engine behaved as one which is normally aspirated.

The dotted line shows the improvement in performance obtained by adding tetra-ethyl lead to D.T.D. 134 fuel (*b*), thus increasing the anti-knock value from 73 to approximately 87–88 octane, C.F.R. Motor Method. In the case of this particular engine the throttle could be fully opened, past the 'gate', at ground level, without the risk of detonation. The performance is improved by about 38% up to the supercharged height (10,500 ft.) or by 16% overall, from ground level to 20,000 ft.

Naturally, the engine manufacturers will always develop their models to take the fullest advantage of any fuel having increased anti-knock value, and, consequently, throttle 'gates' and 'boost' regulation may always be necessary in some form or another in order to control the power output of the engine in relation to the anti-knock value of the fuel. Obviously, the improvement in performance by the use of a fuel of superior anti-knock value will still be shown to the same advantage.

So far as Great Britain is concerned, practically all petroleum products are imported, either in a wholly refined form or as crude. The latter is generally semi-refined before being shipped over. According to the different sources of supply the basic spirits may, and do, vary considerably in their chemical structure and, therefore, anti-knock value. In order to ensure adequate supplies of finished fuels which will be uniform in the latter characteristic, the question of the particular anti-knock material, to be added or blended with the basic spirits, is of some importance and needs careful consideration.

Before discussing the question of actual anti-knock materials it would only be fair to say that there is a home-produced fuel available at the moment, in limited quantities. This is an aviation spirit produced from coal by the low temperature carbonization process, practically the whole production being taken by the Air Ministry. In case of need, the production of coal spirit could undoubtedly be improved, but whether it is possible to produce it in sufficient quantities, and down to a price to compete with spirits directly from crude oil obtained from the various points on the earth's surface, is a matter for conjecture.

The low temperature carbonization process is, as its name implies, a process by which the coal (usually fine coal) is subjected to a 'cooking' procedure in retorts, at relatively low temperature. The latter varies somewhat according to the particular system adopted, but, in general, is between 600° C. and 650° C.

During the process crude oil is produced; this undergoes various treatments, in order to eliminate undesirable constituents, after which suitable aviation grade spirit is obtained from the cleaned-up crude by distillation.

Hydrogenated spirit is now available in Great Britain, but here again it is, at the moment, difficult to foretell how it will affect the situation either from an economical or technical point of view. Hydrogenation is a process in which coal, or oil, is treated with hydrogen at high temperature and pressure in the presence of a catalyst. If coal is used, it is introduced in the form of a paste made by mixing fine coal with a heavy oil or creosote.

Spirit can be produced by this process to give good anti-knock value, and according to the particular conditions employed during the process can have mainly either an aromatic or naphthenic base. The Imperial Chemical Industries Ltd. (I.C.I.) has erected a large hydrogenation plant, and the output is distributed by the major oil companies.

'Cracked' spirits are not, at the moment, used in the manufacture of aviation fuels, principally because 'straight-run' spirits are available in sufficient quantities to meet all needs in this respect. Although they can be stabilized by the addition of special materials, which inhibit gum, it is felt that 'cracked' spirits, used completely as fuels, or blended with other stock, do not offer any particular advantages; particularly, also, since they tend to depreciate in effective anti-knock value under the high duty conditions pertaining in aviation engines, and they have mostly rather poor response to additions of tetra-ethyl lead.

This does not mean that 'cracking' is useless, because, taking the case of automobile fuels, a large majority of these are blended with 'cracked' stocks; in fact little unblended 'straight-run' spirit is used at the present time for such fuels. Since the consumption of automobile fuel far exceeds that of aviation fuel, and 'cracking' should, theoretically, release more 'straight-run' fuel for aviation purposes, the whole question is really one of economics.

It is common knowledge that the anti-knock value of a spirit, disregarding any particular treatment it may receive subsequent to its production from the crude, is largely governed by the particular hydrocarbon group or series which predominate the crude itself. There are three main hydrocarbon groups which characterize petroleum; these are as follows:

(1) Paraffins (C_nH_{2n+2}).
(2) Aromatics (C_nH_{2n-6}).
(3) Naphthenes (C_nH_{2n}).

Their ability to resist detonation varies considerably, and, consequently, aviation spirits produced from crudes having chemical structures conforming to any of the groups mentioned will also vary in anti-knock value.

Having in mind the conditions peculiar to the operation of aviation engines, the order of merit of these hydrocarbon groups, in their ability to resist detonation and/or prevent overheating the cylinders of an engine is as follows:

(1) Naphthenes.
(2) Aromatics.
(3) Paraffins.

At the moment there are practically no spirits available in large quantities or on a commercial basis which will satisfy the needs of the modern high duty aviation engine, so far as anti-knock value is concerned, without the addition of some material to raise this value, because such engines in general require fuels having values between 80 and 87 octane, C.F.R. Motor Method, in order to operate satisfactorily. The highest one can generally expect with a 'straight-run' spirit is about 73 or 74 octane.

Anti-knock Materials.

Before proceeding to consider the merits of the anti-knock materials which are at present used more or less universally and have been adopted by the British Air

Ministry as suitable constituents for aviation fuels, it would be as well to eliminate all discussion concerning alcohols. Not because the alcohols are entirely unsuitable, although they have from time to time been considered, but because they are not as yet used in any way for the make-up of normally obtainable aviation fuels in Great Britain, and in view of the title of this contribution it would be a waste of space to discuss them. Possibly at some future date they may be employed, but one cannot see an immediate use for them in the British picture, particularly when one considers the necessity of providing fuels of uniform quality which can be equally well reproduced and made available over our imperial air routes and for the requirements of the Royal Air Force units which are stationed abroad.

There are two anti-knock materials available in this country which are considered to be suitable for addition to spirits in order to produce satisfactory aviation fuels. These are:

(1) Benzole and/or toluol.
(2) Tetra-ethyl lead.

(1) **Benzole.** Benzole has been used for some years, with success, as an anti-knock material of high value, and although it does not usually detonate in the ordinary sense, it can give rise to severe pre-ignition under appropriate conditions.

Benzole, as is well known, is a coal-tar distillate, being composed of hydrocarbons of the aromatic series; benzene (C_6H_6), toluene (C_7H_8), and xylene (C_8H_{10}). It is produced to a greater extent by the coke-ovens in the steel plants of the country, and to a much lesser extent by the gas works. The total production of crude benzole in the United Kingdom is in the neighbourhood of 50 million gallons, and about 40 million gallons of this are used in a refined form to make up fuels for internal combustion engines.

Although it might be considered as a fuel in itself, benzole is not used alone, for reasons to be explained, but is blended with spirits to form aviation fuels. The amount blended with any spirit depends upon the anti-knock value of the basic spirit used, and upon the final value required.

Blends containing from 10 to 20% of benzole are quite usual, and much larger quantities have been employed.

The main disadvantage to the use of high percentages of benzole in aviation fuels is due to its principal constituent, benzene, which has a freezing-point of about +5° C.; consequently, only relatively small additions, up to a limit of about 20%, can be employed if freezing troubles are to be avoided in the fuel lines and carburettion systems of aircraft engine installations.

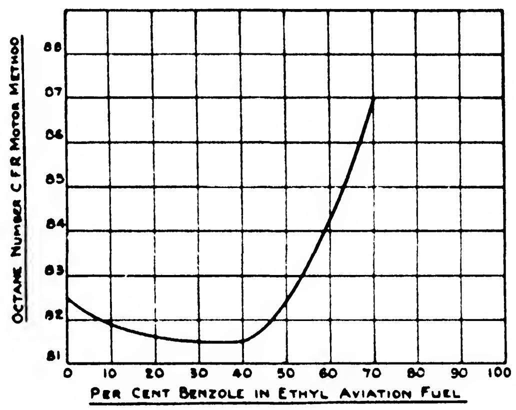
Benzole often depreciates rather badly in effective anti-knock value when subjected to the operating conditions of some high duty engines. In its pure state it has been supposed by many to have an anti-knock value greater than pure octane, but its actual and effective value, when blended with spirits and tested under conditions similar to those employed for aviation fuels, is about the same or less than that of octane. That is to say, its blending value, i.e. its value when amounts up to about 50% are blended with spirits, is lower than that determined arithmetically by taking its apparent anti-knock value into account and assessing the proportionate value of the particular amount added to a spirit. This is clearly shown by the data contained in a paper by Garner and others [7, 1933].

Benzole varies somewhat in behaviour, according to its make-up. That is to say, according to the proportions of its constituents, i.e. benzene, toluene, and xylene, so will its effectiveness as an anti-knock agent vary. Generally speaking, the higher the toluene content, the more effective is its anti-knock value, within certain limits.

Some tests (made by the Wright Aeronautical Corporation with the co-operation of the Standard Oil Co. of New Jersey) were done in America, using a full-scale aviation engine, where it was required to ascertain the amount of benzole necessary to blend with an aviation spirit to equal the performance of the same spirit plus tetra-ethyl lead, both fuels having an octane value of 87, C.F.R. Motor Method. It needed about 75% of benzole in order to obtain this value, and even then the engine would not give its maximum power with the benzole blend, and the specific fuel consumption was considerably raised.

During these tests an interesting fact was discovered in connexion with benzole and tetra-ethyl lead when used together. It was found that in benzole blends, up to about 40%, the lead susceptibility of such blends was considerably reduced. This is shown very clearly in Fig. 2.

FIG 2 BENZOLE SUSCEPTIBILITY CURVE OF AN AVIATION FUEL OF 82.5 OCTANE (C F R MOTOR METHOD) CONTAINING 2.44 MLS PB ET$_4$ PER IMP GALL



(*Reproduced by courtesy of the Standard Oil Co. of New Jersey.*)

From the economic standpoint, and because of its dependence upon the coal and steel industry, benzole is not universally obtainable, except by importation, at many points, outside Great Britain, where machines on our imperial air routes require refuelling or where units of the Royal Air Force are stationed. Even by importation the price is such that the cost of producing aviation fuels containing benzole is very much increased. Therefore, one must consider its usefulness primarily from the point of view of home consumption. In the case of military aviation, and if a state of national emergency, such as war, existed, the supplies of benzole would be considerably restricted for aviation purposes because it would undoubtedly be commandeered for the manufacture of explosives. Toluene, particularly, being the basic raw material for the manufacture of T.N.T.

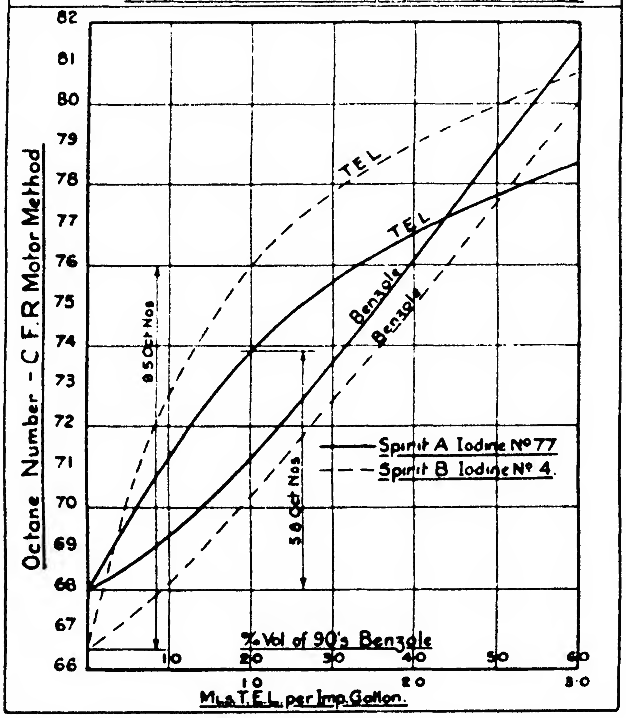
Toluene, itself, is superior to benzole both from the point of view of anti-knock value and in having a low freezing-point (about −95° C.), but it would be even more costly than benzole to produce because it must be 'cut' from benzole. It can, therefore, only be considered for very special purposes.

(2) **Tetra-ethyl Lead.** Tetra-ethyl lead, the characteristics and employment of which have been fully dealt with in a paper before the Royal Aeronautical Society [2, 1934], is

now used to a very large extent in the production of aviation fuels and it is easily obtainable at low cost. Due to its potency, the question of universal supply, in order to treat large quantities of spirit, is simple, because of the very small amounts which need to be added. It may be stored in airtight drums or barrels almost indefinitely.

Its action in the prevention or reduction of detonation and overheating is entirely different to that of benzole. Whereas the latter depends upon its superior anti-knock value in relation to that of the normal spirit, and to the degree of its dilution of that spirit, tetra-ethyl lead may be said to have a specific effect and only uses the spirit as a 'carrier' until it reaches the cylinders of the engine, when, during the combustion process, the 'lead' decomposes and acts chemically upon the fuel/air charge to suppress or eliminate detonation.

FIG 3. CURVE SHOWING RESPONSE OF TEL AND BENZOLE IN FUELS OF DIFFERING CHARACTERISTICS



(*Reproduced from paper entitled 'Ethyl', by F. R. Banks, 'Journ. Royal Aëronautical Soc.', April 1934.*)

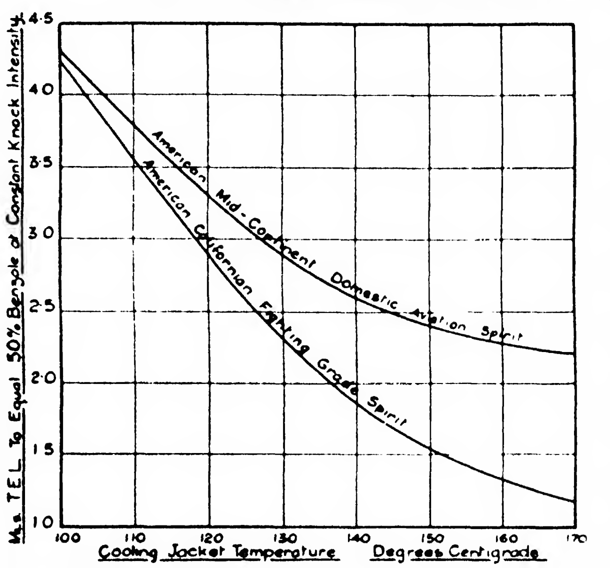
The effectiveness of tetra-ethyl lead is also dependent upon its concentration in a spirit, but because it is not a fuel and may be called a chemical knock suppressor, and since its action is specific, there is therefore usually a limit to the concentration which can be usefully employed, the degree of concentration depending upon the basic spirit used.

This explains the characteristic difference in the shapes of the knock-rating curves between fuels having various benzole contents and lead concentrations.

To sum up, increasing benzole concentrations in a spirit tend to show progressive increase in the anti-knock value of the resultant fuel, whereas with increasing concentrations of tetra-ethyl lead this increase becomes progressively less. These characteristics are shown very clearly in Fig. 3, in which benzole and also tetra-ethyl lead have been added, separately, to two spirits which vary considerably in their chemical characteristics, one being 'straight run' of naphthenic base and the other highly 'cracked'.

A very important feature with regard to the relative behaviour of leaded fuels and benzole blends is that the former retain their effective anti-knock values to a high degree when subjected to high duty conditions, such as those pertaining particularly in high performance aircraft engines, whereas the latter drop off rather badly in this respect under similar conditions. This effect is clearly shown in Fig. 4.

FIG 4 VARIATION OF BENZOLE-T.E.L. RATIO IN AVIATION GASOLINES DUE TO CHANGE OF ENGINE TEMPERATURE



(*Reproduced from paper entitled 'Ethyl', by F. R. Banks, 'Journ. Royal Aëronautical Soc.', April 1934.*)

The addition of tetra-ethyl lead to a spirit does not measurably alter its physical characteristics, such as distillation range, freezing-point, and specific gravity, &c.

The two materials discussed are so far considered to be the most generally available anti-knock agents in this country. However, recent developments in America have produced two valuable blending agents for the make-up of fuels of high anti-knock value. These are iso-octane and di-isopropyl ether.

C.P. Iso-octane has, of course, been employed for some years as a primary standard reference fuel, but its use has been restricted to that of knock-rating tests owing to its high cost of production. Two major oil concerns, namely, the Standard Oil Company of New Jersey and the Shell, have, however, been able to produce commercial iso-octane in relatively large quantity and down to a cost which allows it to be seriously considered as a constituent of aviation fuel. Aviation fuel containing iso-octane is already being used in America by the U.S. Army Air Corps and the U.S. Navy, Commercial aviation operating companies are also seriously considering its use.

Iso-octane is at the moment only employed as a constituent of 100 octane fuel, which is a fuel having an octane number of 100 when tested by the method evolved by the U.S. Army Air Corps, Material Division, Wright Field, Dayton. The fuel consists of approximately 50% of a good aviation gasoline blended with the balance of iso-octane, plus about 3·4–4·0 ml. of tetra-ethyl lead per Imperial gallon.

So far the U.S. Army knock-test method appears to be a satisfactory one for fuels having octane numbers in excess of 87, and this 100 octane fuel is equivalent to between 96 and 98·5 octane C.F.R. Motor Method. The reader is referred to two important papers by Klein [9, 1936; 10, 1935] and a letter signed by Cronstedt and others [6, 1935].

The British Air Ministry has issued a provisional specification for such a fuel so that it may be tried out experimentally by the engine manufacturers and certain squadrons in the R.A.F. This fuel must, at the moment, be imported into Great Britain, but if these experiments by the Air Ministry are successful there is little doubt that other manufacturing arrangements will be made. Unfortunately the bulk production of iso-octane largely depends upon the cracking industry, and America is very happily placed regarding this, but there is little cracking carried out in Great Britain.

The raw material for the manufacture of iso-octane is iso-butylene, which is present in small amounts in the refinery gases. This is converted into di-iso-butylene by one of several processes, and the latter is hydrogenated (either by the low- or high-pressure system) to yield iso-octane.

Di-isopropyl ether is the most recent development in the synthesis of fuels on a commercial production basis. It is an excellent anti-knock material having a good response to additions of tetra-ethyl lead, and its potentialities from the production aspect appear to be far greater than those of iso-octane. Di-isopropyl ether was first found for this purpose by Buc, who has, with Aldrin, presented a paper describing its features and uses [4, 1936].

The raw material from which this material is produced is propylene, present in refinery gases (or made by cracking propane from natural gas). Propylene, under appropriate chemical treatment, reacts to form di-isopropyl ether, which is a branched-chain ether.

According to Buc and Aldrin di-isopropyl ether, when blended in ordinary aviation gasolines, will produce a fuel of 100 octane (U.S. Army Air Corps test) with a tetra-ethyl lead concentration not exceeding 3 ml. per U.S. gallon (3·6 ml. per imperial gallon). Heron [8, 1936] has reported the octane number of di-isopropyl ether as 98·5 Army Method, and from the evidence available (Buc and Aldrin) it appears to have a slightly superior blending value than that of technical iso-octane, and is also superior for a given lead concentration in corresponding blends.

Di-isopropyl ether has, however, one important disadvantage, which is its relatively low calorific value. This is some 20% less than that of iso-octane, and when used in the quantity (about 40% by volume) necessary to make up 100 octane fuel, the resultant blend is about 7% lower in calorific value than that of a similar fuel employing iso-octane. Actually, di-isopropyl ether is not intended to take the place of iso-octane as a blending agent but rather to be complementary or supplementary to it, and since it offers good production potentialities it is bound to receive serious consideration by all concerned in the use and distribution of high octane-number fuels.

One important point regarding these two blending agents (iso-octane and di-isopropyl ether) is, that their inclusion in a fuel, in amounts from 40% up to 50% by volume, will render the finished fuel deficient in 'light ends' for the normal carburetter-type engine. Therefore it is usually necessary to add some material which boils at a somewhat lower temperature; for this purpose iso-pentane is generally used.

(*b*) Distillation Characteristics.

The distillation characteristics of an aviation fuel are most important because upon them depend the good starting, smooth functioning, and fuel economy of an engine (assuming, naturally, that the anti-knock value is satisfactory.)

The distillation range should be well proportioned in order to satisfy the requirements of the various distribution arrangements met with on different types of engines. Experience has shown that the temperatures at which 10%, 50%, and 90% of a fuel is recovered by distillation are generally the controlling factors determining its suitability in respect of the conditions previously mentioned.

The 10% point controls the starting characteristics and is an index of the tendency to vapour lock when taken in conjunction with vapour pressure; it is therefore necessary to avoid too large proportions of the low-boiling constituents in order to eliminate the tendency of premature vaporization in the fuel lines and carburettors, which leads to vapour locking. The temperature limits within which the 10% point should lie are 63–75° C.

The 50% point is a measure of the ability of the fuel to provide rapid warming up and good acceleration of the engine. To ensure this desired flexibility, at least 50% of the fuel should be recovered before the thermometer reads 100° C.

The 90% point controls the proportions of the higher boiling constituents present in the fuel, and this should not be too widely separated from the 50% point, otherwise the presence of an excess of these constituents will affect good distribution and fuel economy adversely. The temperature limits for this point should be between 125° C. and 150° C., but preference is usually given to a fuel the 90% point of which is nearer to the lower temperature limit.

The initial boiling-point and also the end-point of the fuel are not mentioned because many tests have proved conclusively that neither has any significance when related to engine performance.

(*c*) Vapour Pressure.

Vapour pressure and the 10% point combine to control the vapour-locking tendency of a fuel. The Reid vapour-pressure test, which now appears to be universally accepted, is a simple method of determining this characteristic of fuels. It is an arbitrary test and, therefore, the results are not absolute. They give, however, an accurate and easily reproducible estimate of this quality, the limit of which has previously been determined by practical experience. Some engine installations are particularly bad as regards susceptibility to vapour lock, and in the case of high duty engines, particularly, the engine-driven fuel pumps, due to their proximity to the engine, sometimes work at relatively high temperatures and vapour locking has occurred on the 'inlet' side of these pumps. The Reid vapour-pressure value for a satisfactory fuel should not, in general, exceed 7·0 lb. per sq. in.

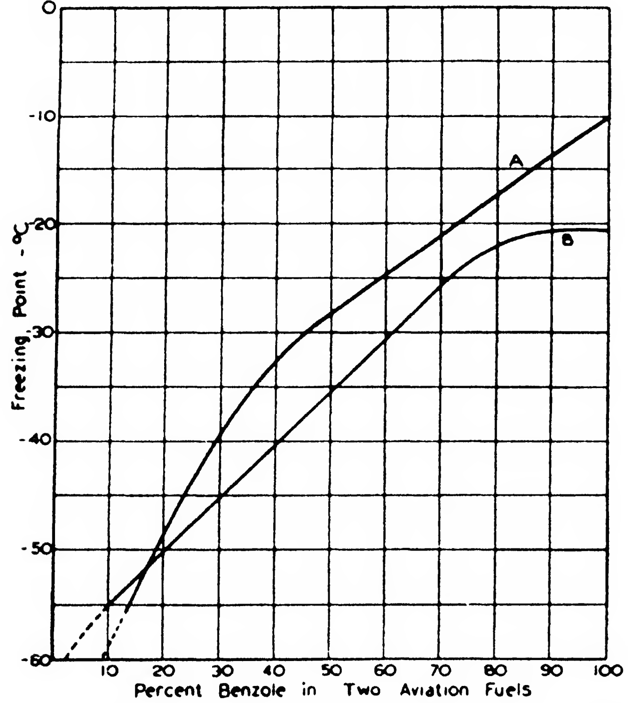
(*d*) Freezing-point.

The provision of a low freezing-point is very important for aviation fuels because of the ability of modern aircraft to operate at high altitudes, and also because they must function equally satisfactorily in atmospheric conditions of varying temperature and humidity.

In the case of all ordinary spirits and the aviation fuels produced from them by the addition of tetra-ethyl lead, there is little or no risk of the fuel freezing in the fuel lines or carburettor passages. But as regards fuels containing benzole, there is considerable risk of freezing occurring, and unless its use is very much restricted it is not possible to meet the freezing-point requirements. The relatively high freezing-point of benzole also is a great drawback to its use as an anti-knock material because only such small quantities can be used.

The curves in Fig. 5 show the effect of various benzole blends upon the freezing-point. Two benzoles, differing in respect of the proportions of their constituents, were added to typical aviation grade spirits. The curves give the freezing-points, as determined by the formation of the first benzene crystals, of the resultant fuels obtained by blending each benzole with an aviation spirit. Fuel *A* was made up with a benzole having a lower toluol and higher benzene content than fuel *B*.

FIG. 5. - FREEZING POINT CHART.



Although the freezing-point of a fuel is exceedingly important and must be specified for the reasons previously stated, this does not mean that freezing troubles will be avoided with a fuel having a low freezing-point, although this in itself is particularly important in preventing solids forming in the fuel system. Freezing at or immediately above the carburettor chokes, however, is possible and, unfortunately, often usual under certain conditions, with fuels having low freezing-points and which contain no benzole at all.

If the humidity is high, the moisture in the air can freeze on the throttle and walls where the venturi choke widens into the carburettor riser. This does not always occur at zero atmospheric temperature conditions, but rather it is due to a specific combination of humidity temperature and latent heat of the fuel/air mixture. In this connexion, the rapid evaporation which takes place, due to a disproportionate percentage of volatile constituents in the fuel, will aggravate the condition by more rapid diminution of the temperature.

An attempt has been made in America (where, incidentally, benzole has been little used and has now been definitely abandoned) to alleviate this difficulty by stating the minimum acceptable for the sum of the temperatures of the 10%, and 50%, and specifying an aggregate of not less than 307° F. (153° C.). However, this can only be regarded as means to alleviate, but not to cure, the trouble.

Further alternatives to deal with this trouble which have been found efficacious are: (1) to 'bleed' alcohol into the venturi throat. (Alcohols are soluble in water and alcohol/water mixtures have freezing-points below that of water alone. The action of an alcohol, used in the former manner, (1), appears to be that when it contacts with the ice, the freezing-point of the mixture so formed is lowered, which causes the ice to melt and almost immediately to become soft and non-adherent.) (2) Heating the carburettor riser about the choke and throttle levels by means of a hot-oil jacket, and (3) heating the air intake of the carburettor.

Two informative papers have been written on this whole matter, and the reader is referred to them for more detailed information [1, 1934], [5, 1935].

(*e*) Freedom from Sulphur.

The presence of sulphur in excess may cause corrosion troubles in the fuel system, and therefore the sulphur content of a fuel is usually limited.

The base spirit and the finished fuel must not contain free sulphur, and, in the combined form, the total sulphur content should not, in general, exceed 0·10% by weight, although in most aviation fuels this is usually kept between 0·02% and 0·05%.

(*f*) Freedom from Gum.

The care which is taken by the refiners of modern spirits, and also the limitations and tests imposed upon the former by aviation fuel specifications, is such that no troubles arising from gum formation, either in the case of fuel storage or in the engine installation, need be anticipated. This is principally due to the fact that many modern specifications are so written to exclude 'cracked' spirit blends, and a spirit which passes the accelerated ageing test may be considered to be entirely satisfactory so far as its stability is concerned. The British Air Ministry specifications for Aviation Fuels permit the use of cracked spirits provided the accelerated ageing test is met.

The accelerated ageing test, where the spirit sample is placed in a bomb with oxygen at 100 lb. per sq. in. for 4 hours at a temperature of 100° C., is done to determine the potential gum and the stability of the spirit under storage conditions. The existent gum test consists of evaporating completely 100 ml. of the oxidized sample in a glass dish. The maximum amount of gum formed after evaporation is usually limited to 10 mg. (per 100 ml.).

The British Air Ministry test for potential gum consists of incubating the sample in the dark for 20 hours at 35° C., after which it is evaporated in a similar manner to the test for existent gum.

The acid heat test is often used in America, in addition to the accelerated ageing test, as a simple determination for the presence of 'cracked' stock.

A description of this test may be of interest here; the apparatus consists of an ordinary thermos or vacuum flask fitted with the usual screwed metal cap and supplied with two tapered cork stoppers, both impregnated with paraffin wax; one stopper is vented with a hole. Finally, a thermometer is included in the equipment. The reagent is commercial sulphuric acid having a specific gravity of not less than 1·834 and not greater than 1·838.

The procedure is as follows: 150 ml. of the fuel to be tested is measured into the vacuum flask at approximately room temperature and its temperature recorded after being in the flask for 2 minutes. 30 ml. of the sulphuric acid having the same temperature as the fuel are then poured into the flask, the vented cork stopper inserted, and the flask agitated gently for 1 minute, after which the temperature of the acid layer is taken. If the thermometer shows a temperature rise of as much as 15° C. (27° F.), the sample fails and the test is discontinued at this point.

If the temperature rise during the preliminary mixing is less than 15° C., the unvented cork stopper is inserted and the metal cap of the flask screwed on to hold the cork firmly in place. The flask is then shaken for 2 minutes, at the end of which period the temperature of the acid layer is taken again.

The difference between the initial and final temperature readings is recorded as the acid heat of the fuel. The preliminary mixing described in a previous paragraph is a safety measure to eliminate highly 'cracked' samples which might develop excessive pressures when shaken in the bottle with the unvented cork stopper. The specifications in America which include this test stipulate that the acid heat of the sample must not be above 11° C. to pass.

The British Air Ministry Aviation Fuel Specifications

These specifications are reproduced at the end of this contribution in the form of Appendices A and B. They are complete in themselves and specify recognized test procedures, employed in this country, which have been evolved by the Institution of Petroleum Technologists in collaboration with the Air Ministry.

It is not proposed here to discuss the individual tests adopted to meet the various requirements of these fuels because they are published in detail by the I.P.T. and follow defined lines. For instance, the description of the C.F.R. Motor Method of ascertaining the anti-knock value is given in detail elsewhere in this work. However, because the question of the *effective* anti-knock value of an aviation fuel is of paramount importance, it is advisable to discuss the relationship between the value given to a fuel in the knock-testing engine and its performance in a full-scale aviation engine, in order that the reader will have some idea of the problems which confront those whose work it is to formulate fuel specifications.

Before doing this it would be as well to emphasize the essential differences between the A.M. D.T.D. 224 and 230 specifications. In the case of the former, it will be noted that this does not include tetra-ethyl lead, but only allows the use of added aromatics up to a limit governed by the freezing-point of the finished fuel. In order to obtain the necessary anti-knock value and to allow reasonable additions of aromatics to the various base spirits employed, a freezing-point of not higher than −50° C. has been chosen. This is 10° C. higher than that laid down for the D.T.D. 230 fuel. Fuel to D.T.D. 224 specification is used only for those types of engines in service which are unable to take advantage of tetra-ethyl lead.

The D.T.D. 230 specification allows the use of tetra-ethyl lead up to a maximum concentration of 4 ml. per imperial gallon. Added aromatics are also allowed, provided that the freezing-point of the finished fuel is, in this case, not higher than −60° C.

In issuing these specifications the Air Ministry has departed from its previous practice of having only one fuel available for all purposes. The provision of two fuels is a very satisfactory method of meeting the needs of the various types of engines in service. All new engines for the Royal Air Force must, however, be developed on a D.T.D. 230 fuel, which contains tetra-ethyl lead, otherwise they will not be accepted.

Although these specifications may vary somewhat in detail to the conditions discussed in the previous section of this contribution, it must be borne in mind that the Air Ministry, in formulating them, had many other considerations to take into account in order to provide fuels having good 'average' qualities from basic spirits which were available in sufficient quantities to meet the needs of the R.A.F. at home and abroad, or where British engines are used in machines operating our imperial air routes. For instance, it will be noticed that both specifications allow an upper limit, for sulphur content, of 0·15% by weight. This is an increase of 0·05%, for that which is normally considered should be the maximum, i.e. 0·10%, but it was necessary to do this in order to include base spirits which are obtainable in adequate quantities, but in which the sulphur content is somewhat higher than usual.

The Problem of Correlating Knock Tests with Operating Conditions

The anti-knock value in terms of octane number of any fuel depends upon the test method employed, and therefore such number cannot be considered an 'absolute' one when applied to engine operation. Consequently, because it is difficult to simulate, in a laboratory knock-testing engine, those conditions peculiar to the operation of a full-scale aviation engine, the problem of correlating laboratory results with practical operation is one of considerable difficulty; all the more so when the different types of aviation engines are taken into account.

Therefore, since it is impracticable to have a number of different fuel-test methods to suit all engines, one must be content with a set of conditions which will provide good average correlation over a fairly wide range of operating conditions.

It is exceedingly difficult to decide how to run correlation tests and whether full-scale or single-cylinder units of aviation engines should be used when endeavouring to ascertain the effective anti-knock values of different fuels, because there is no really satisfactory method, at the moment, for the accurate detection of the commencement of detonating conditions in this class of engine. In the case of aviation engines, particularly, audible detonation is by no means always apparent, but a dangerous rise of the cylinder-head temperature is often the first manifestation of trouble. This is particularly so in the case of large air-cooled engines.

Prior to the formulation of the D.T.D. 224 and 230 specifications, the British Air Ministry in co-operation with the Sub-Committee on the Knock Rating of Aviation Fuels, which was set up by the I.P.T., carried out a number of tests with single cylinder-aviation engine units of air- and water-cooled types, in conjunction with the C.F.R. fuel-test engine, in order to find a set of test conditions, for fuels, which would enable good correlation to be obtained with the various aviation engine types in service. As a result of this work, a modification of the 'Motor Method' test was found to give correlation and was adopted by the Air Ministry for its fuel specifications. These tests were very clearly and completely described by Pye in a report read before the World Petroleum Congress, held in London [11, 1933]. It, however, took into account only those fuels of moderate anti-knock value, i.e. between 70 and 80 octane, and did not include any which contained tetra-ethyl lead, although the sub-standard reference fuels were leaded.

In America correlation tests have been done at the works of the various aviation-engine manufacturers on full-scale engines, to a programme laid down by the C.F.R. Aviation Gasoline Detonation Sub-Committee, in order to obtain a satisfactory test method for the C.F.R. engine. This work has been recorded by Veal in the paper referred to at the end of this article [13, 1936]. As the result of a very comprehensive investigation the C.F.R. Motor Method test is retained for rating aviation fuels up to and including 87 octane number.

As to the question of employing full-scale or single-cylinder engines, the use of the former would appear to be more satisfactory if a complete survey of a number of fuels is contemplated. The results will be more comprehensive and valuable because they take into account the characteristics of different engines, and this is a most important consideration when investigating the relative merits of fuels. Full-scale tests are, however, exceedingly expensive and take a great deal of time to complete. The American tests took nearly 1 year to do 50% of the prescribed work.

Tests on single-cylinder units are, obviously, cheaper, but it is often difficult to tell whether the results obtained are satisfactory until the fuels, evolved as the result of such tests, have been used in service for some time and in a number of different engines.

It is not proposed here to describe the particular methods of test adopted, but the papers referred to previously [5, 6] give a good idea of two distinct means of doing this correlation work. There is one important condition in favour of running full-scale tests, which cannot be accurately reproduced in single-cylinder work; this is, the effect which the multi-cylinder induction system has upon running conditions with different fuels.

A 'consumption loop', i.e. a curve produced by plotting the specific fuel consumption (lb. per B.H.P.hr.) against brake mean effective pressure (B/M.E.P.), should always be made with every fuel tested, together with cylinder-head and barrel temperatures, in order to determine the weakest mixture strength at which each fuel will operate satisfactorily without detonation or overheating becoming serious.

Fuels which have the same octane number but which have different chemical characteristics, distillation range, and, perhaps, contain different amounts of tetra-ethyl lead or benzole, do not always have similar effective values under full-scale operating conditions. Obviously, therefore, the superior fuel is that which gives smooth running, without detonation or overheating and with the best economy under these conditions.

In the case of the single-cylinder engine, and due to its relatively simple induction system, it is often possible to reduce the mixture strength to a greater extent than is normally so with the full-scale engine, and in consequence the results may be rather misleading. It is particularly so when attempting to do this at full throttle or at maximum permissible 'boost' rather than at reduced load or cruising conditions. While economy under cruising conditions is more important than at full load, correlation work should be done under the latter conditions because the engine will be more sensitive to changes in fuel characteristics. Detonation free operation at full throttle, or at maximum permissible 'boost', is absolutely necessary, particularly for full-load 'take off' and also for climbing, but the mixture strength may be increased for these conditions.

Fuels chosen in this manner and subsequent supplies which have been tested in the laboratory under conditions evolved as the result of the full-scale tests, will probably give good results when tuning production aviation engines for best economy at cruising power.

APPENDIX A

D.T.D. 224

Crown Copyright Reserved

August, 1933

AIR MINISTRY MATERIAL SPECIFICATION

77 OCTANE STANDARD FUEL FOR AERO-ENGINES

1. Description

The standard fuel for aero-engines shall consist of high-grade petrol prepared from crude petroleum, coal spirit or mixtures thereof.

The fuel as a whole shall be neutral, clear, free from undissolved water, and any suspended matter.

In order to obtain the necessary anti-detonation value as specified in Clause 8, it is permissible to add aromatic hydrocarbons, the extent of such additions being governed by the succeeding clauses of this specification.

2. Distillation Range

When 100 mls. of the fuel submitted are distilled in the standard distillation apparatus, there shall distil at 760 mm. pressure:—

Below 75° C. not less than 10 per cent.
At 100° C. not less than 50 per cent.
At 150° C. not less than 90 per cent.
The end point shall not exceed 180° C.
The distillation loss shall not exceed 2 per cent.
The total volume of distillate collected in the receiver shall not be less than 96 per cent.

3. Vapour Pressure

The vapour pressure as determined by the Reid method at 37·8° C. (100° F.) shall not exceed 7 lb. per square inch.

4. Specific Gravity

The specific gravity at 15° C. shall be not more than 0·79.

5. Sulphur Content

There shall be a complete absence of free sulphur when determined by the copper strip method and the total sulphur content shall not exceed 0·15 per cent. by weight.

6. Freezing Point

The freezing point as indicated by the initial formation of solid shall be not higher than minus 50° C.

7. Gum

(*a*) *Existent Gum.*—The amount of existent gum as determined by the evaporative method in a glass dish shall not exceed 10 mgms. per 100 ml.

(*b*) *Potential Gum.*—After 50 mls. of the fuel have been incubated at 35° C. for 20 hours, the increase of gum yield over and above the existent gum as determined by the evaporative glass dish method shall not exceed 10 mgms. per 100 ml. (For method of determination of gum, *see* Appendix 1.)

8. Anti-Detonation Value

The anti-detonation value shall be not less than 77 octane number when determined by the standard 'C.F.R. MOTOR METHOD' modified so that the unit is run with a mixture temperature of 260° F.

The octane number is numerically the percentage by volume of iso-octane (2, 2, 4 tri-methyl pentane) in a mixture of iso-octane and normal heptane. The octane number of the fuel is the octane number of the mixture of iso-octane and normal heptane which it matches in anti-detonation value.

A secondary or sub-standard reference fuel may be used for purposes of matching, but the sub-standard fuel must be equal in knock rating to the primary octane-heptane mixture when tested under the conditions specified. Supplies of standard or sub-standard fuels will not be issued by the Air Ministry. The Air Ministry will use as a sub-standard, a straight run petrol of high knock rating with the addition of pure crystallisable Benzene.

(*Note.*—Three comparisons of the sample with the reference fuel are to be made. The sample on the average of these comparisons shall not be inferior to the standard. Frequent calibrations of the secondary reference fuels against the primary octane-heptane standard must be made.)

9. Methods of Test

Except where otherwise stated, the 'Standard Methods of Testing Petroleum and its Products', Second Edition, and such Addenda as may be promulgated by the Institution of Petroleum Technologists will be used. The required tests are enumerated in Appendices 1 and 2.

10. Sampling

Normal I.P.T. methods of sampling are to be adopted; but in cases of dispute, particularly in connection with gum tests, it is essential that sampling should be carried out in accordance with the details laid down in Appendix 3.

APPENDIX 1

Gum Tests.—Description

Apparatus

The apparatus shall consist of the following:—

(*a*) *Dish.*—The dish shall be made of a suitable resistance glass, and in shape shall be either hemispherical, 80 to 90 mm. in diameter, or flat-bottomed, 80 to 90 mm. in diameter at the top, 45 to 50 mm. in depth, and approximately 45 mm. in diameter at the bottom.

(*b*) *Steam Bath.*—The apertures shall be of such size that the dishes will be immersed to within about 10 mm. of the top. If the evaporation is not carried out in a draught-free chamber, the bath shall be provided with a draught shield.

(*c*) *Storage Flask.*—A 500 ml. measuring flask fitted with a glass stopper, and made of a suitable resistance glass, shall be used.

Procedure

Existent Gum.—Fifty ml. of the petrol shall be evaporated in the glass dish on a vigorously-boiling steam bath, the dish having been cleaned previously by soaking in chromic-acid solution, and rinsing in distilled water.

After the evaporation, the outside of the dish shall be wiped dry; the dish shall then be transferred to an oven maintained at 150° C. and allowed to remain there for one hour. After cooling in a dust-free place for 20 minutes, the dish shall be weighed by tare, against another similar dish which has been treated similarly but without the petrol, to an accuracy of ±0·1 mgm. The operations after heating the dish shall be made with the use of metal forceps.

Potential Gum.—Fifty ml. of the petrol contained in the glass-stoppered glass flask shall be incubated at 35° C. in the dark for 20 hours. At the end of that time, the contents of the flask, together with acetone rinsings obtained by swilling out the emptied flask with a little re-distilled acetone, shall be transferred to the glass dish described in the previous test, and the amount of gum formed determined by the evaporative method described previously.

APPENDIX 2

Schedule of Standard I.P.T. Tests

Specific Gravity	G. 1.
Distillation	G. 3.
*Total Sulphur	G. 4 (A.S.T.M. D. 90–30T).
*Free Sulphur	G. 4.B (A.S.T.M. D. 130–30).
*Vapour Pressure	G. 37 (A.S.T.M. D. 323–32T).
*Normal Sampling ..	I.P.T. (A.S.T.M. D. 270–30T).
*Anti-Detonation Value	G. 39 (A.S.T.M. D. 357–33T).

* *Note.*—These tests are either under consideration or revision by the Institution of Petroleum Technologists and pending the issue of the I.P.T. addenda concerned the equivalent A.S.T.M. methods enumerated must be used.

APPENDIX 3

Method of Sampling for Gum Tests

It is important that the following precautions be taken in sampling in order to avoid the introduction of extraneous matter which might cause erratic gumming:—

(*a*) The bottles, preferably narrow-necked and glass stoppered, should be washed in chromic-acid solution, then rinsed with distilled water, and dried.

(*b*) If corks are used, these should be new and extracted with acetone and preferably wrapped around with tin or lead foil.

(*c*) The glass dipper, or syphon, etc., used for removing the sample from the container, should be frequently rinsed with acetone and dried in order to remove any gum.

(*d*) The sample bottle should be (i) filled to the neck, (ii) wrapped or packed in a light-proof container, and (iii) stored in a cool place until required for analysis.

APPENDIX B

D.T.D. 230

Crown Copyright Reserved

August, 1933

AIR MINISTRY MATERIAL SPECIFICATION

87 OCTANE STANDARD FUEL FOR AERO-ENGINES

1. Description

The standard fuel for aero-engines shall consist of high-grade petrol prepared from crude petroleum, coal spirit or mixtures thereof.

The fuel as a whole shall be neutral, clear, free from undissolved water, and any suspended matter.

In order to obtain the necessary anti-detonation value as specified in Clause 8, it is permissible to add aromatic hydrocarbons and/or tetra-ethyl lead in the form of 1T ethyl fluid in concentrations not exceeding 4 mls. of tetra-ethyl lead per Imperial gallon.

The extent of such additions will be governed by the succeeding clauses of this specification.

2. Distillation Range

When 100 mls. of the fuel submitted are distilled in the standard distillation apparatus, there shall distil at 760 mm. pressure:—

Below 75° C. not less than 10 per cent.
At 100° C. not less than 50 per cent.
At 150° C. not less than 90 per cent.
The end point shall not exceed 180° C.
The distillation loss shall not exceed 2 per cent.
The total volume of distillate collected in the receiver shall not be less than 96 per cent.

3. Vapour Pressure

The vapour pressure as determined by the Reid method at 37·8° C. (100° F.) shall not exceed 7 lb. per square inch.

4. Specific Gravity

The specific gravity at 15° C. shall be not more than 0·79.

5. Sulphur Content

There shall be a complete absence of free sulphur when determined by the copper strip method and the total sulphur content shall not exceed 0·15 per cent. by weight.

6. Freezing Point

The freezing point as indicated by the initial formation of solid shall be not higher than minus 60° C.

7. Gum

(*a*) *Existent Gum.*—The amount of existent gum as determined by the evaporative method in a glass dish shall not exceed 10 mgms. per 100 ml.

(*b*) *Potential Gum.*—After 50 mls. of the fuel have been incubated at 35° C. for 20 hours, the increase of gum yield over and above the existent gum as determined by the evaporative glass dish method shall not exceed 10 mgms. per 100 ml. (For method of determination of gum, *see* Appendix 1.)

8. Anti-Detonation Value

The anti-detonation value shall be not less than 87 octane number when determined by the standard 'C.F.R. MOTOR METHOD' modified so that the unit is run with a mixture temperature of 260° F.

The octane number is numerically the percentage by volume of iso-octane (2, 2, 4 tri-methyl pentane) in a mixture of iso-octane and normal heptane. The octane number of the fuel is the octane number of the mixture of iso-octane and normal heptane which it matches in anti-detonation value.

A secondary or sub-standard reference fuel may be used for purposes of matching, but the sub-standard fuel must be equal in knock rating to the primary octane-heptane mixture when tested under the conditions specified. Supplies of standard or sub-standard fuels will not be issued by the Air Ministry. The Air Ministry will use as a sub-standard, a straight run petrol of high knock rating with the addition of pure crystallizable Benzene when undoped fuels are being tested and the addition of T.E.L. when fuels containing T.E.L. are being tested.

(*Note.*—Three comparisons of the sample with the reference fuel are to be made. The sample on the average of these comparisons shall not be inferior to the standard. Frequent calibrations of the secondary reference fuels against the primary octane-heptane standard must be made.)

9. Colour

When tetra-ethyl lead is used as an anti-detonant, the fuel must be coloured noticeably blue with a suitable dye to distinguish the leaded fuel from those not so doped.

10. Methods of Test

Except where otherwise stated, the 'Standard Methods of Testing Petroleum and its Products', Second Edition, and such Addenda as may be promulgated by the Institution of Petroleum Technologists will be used. The required tests are enumerated in Appendices 1 and 2.

11. Sampling

Normal I.P.T. methods of sampling are to be adopted; but in cases of dispute, particularly in connection with gum tests, it is essential that sampling should be carried out in accordance with the details laid down in Appendix 3.

APPENDIX 1

Gum Tests.—Description

Apparatus

The apparatus shall consist of the following:—

(*a*) *Dish.*—The dish shall be made of a suitable resistance glass, and in shape shall be either hemispherical, 80 to 90 mm. in diameter, or flat-bottomed, 80 to 90 mm. in diameter at the top, 45 to 50 mm. in depth, and approximately 45 mm. in diameter at the bottom.

(*b*) *Steam Bath.*—The apertures shall be of such size that the dishes will be immersed to within about 10 mm. of the top. If the evaporation is not carried out in a draught-free chamber, the bath shall be provided with a draught shield.

(*c*) *Storage Flask.*—A 500 ml. measuring flask fitted with a glass stopper, and made of a suitable resistance glass, shall be used.

Procedure

Existent Gum.—Fifty ml. of the petrol shall be evaporated in the glass dish on a vigorously-boiling steam bath, the dish having been cleaned previously by soaking in chromic-acid solution, and rinsing in distilled water.

After the evaporation, the outside of the dish shall be wiped dry; the dish shall then be transferred to an oven maintained at 150° C. and allowed to remain there for one hour. After cooling in a dust-free place for 20 minutes, the dish shall be weighed by tare, against another similar dish which has been treated similarly but without the petrol, to an accuracy of ±0·1 mgm. The operations after heating the dish shall be made with the use of metal forceps.

Potential Gum.—Fifty ml. of the petrol contained in the glass-stoppered glass flask shall be incubated at 35° C. in the dark for 20 hours. At the end of that time, the contents of the flask, together with acetone rinsings obtained by swilling out the emptied flask with a little re-distilled acetone, shall be transferred to the glass dish described in the previous test, and the amount of gum formed determined by the evaporative method described previously.

APPENDIX 2

Schedule of Standard I.P.T. Tests

Specific Gravity	G. 1.
Distillation	G. 3.
*Total Sulphur	G. 4 (A.S.T.M. D. 90-30T).
*Free Sulphur	G. 4.B (A.S.T.M. D. 130-30).
*Vapour Pressure	G. 37 (A.S.T.M. D. 323-32T).
*Normal Sampling ..	I.P.T. (A.S.T.M. D. 270-30T).
*Determination of Tetra Ethyl Lead	G. 38 (Edgar & Calingaert).
*Anti-Detonation Value	G. 39 (A.S.T.M. D. 357-33T).

* *Note.*—These tests are either under consideration or revision by the Institution of Petroleum Technologists and pending the issue of the I.P.T. addenda concerned the equivalent A.S.T.M. methods or alternative methods enumerated must be used.

APPENDIX 3

Method of Sampling for Gum Tests

It is important that the following precautions be taken in sampling in order to avoid the introduction of extraneous matter which might cause erratic gumming:—

(*a*) The bottles, preferably narrow-necked and glass stoppered, should be washed in chromic-acid solution, then rinsed with distilled water, and dried.

(*b*) If corks are used, these should be new and extracted with acetone and preferably wrapped around with tin or lead foil.

(*c*) The glass dipper, or syphon, etc., used for removing the sample from the container, should be frequently rinsed with acetone and dried in order to remove any gum.

(*d*) The sample bottle should be (i) filled to the neck, (ii) wrapped or packed in a light-proof container, and (iii) stored in a cool place until required for analysis.

REFERENCES

1. Allen, H. H., Rodgers, G. C., and Brookes, D. C. *J.S.A.E.* **35**, 417 (1934).
2. Banks, F. R. *J.R. Aë. Soc.* **38**, 309 (1934).
3. Bass, E. L. *Aircraft Engineering*, **6**, 320 (1934).
4. Buc, H. E., and Aldrin, E. E. *J.S.A.E.* **39**, 333 (1936).
5. Clothier, W. C. *Proc. R. Aë. Soc.* **39**, 761 (1935).
6. Cronstedt, V., DuBois, R. N., Klein, F. D., and Heron, S. D. *J. Aeronautical Sciences*, **2**, 125 (1935).
7. Garner, F. H., Evans, E. B., Sprake, C. H., and Broom, W. E. J. *World Petr. Cong. London*, July 1933, **2**, 170.
8. Heron, S. D. *J.S.A.E.* **39**, 310 (1936).
9. Klein, F. D. *J.S.A.E.* **39**, 304 (1936).
10. —— *J. Aeronautical Sciences*, **2**, 43 (1935).
11. Pye, D. R. *World Petr. Cong. London*, July 1933, **2**, 186.
12. Taylor, E. S. *Aircraft Engineering*, **5**, 136 (1933).
13. Veal, C. B. *J.S.A.E.* **38**, 161 (1936).

BIBLIOGRAPHY

The Internal Combustion Engine, vols. 1 and 2, by D. R. Pye.
The High Speed Internal Combustion Engine, vol. 2, by H. R. Ricardo.

AVIATION FUELS—FRENCH PRACTICE

By Dr. P. DUMANOIS, Hon. M.Inst.P.T.
Inspector-General of Aeronautics, France

Before detonation and octane numbers were known, aviation companies used the distillation curve in order to select and evaluate fuels. Systematic trials of fuels in engines showed that those with low distillation ranges were the most useful; the choice of distillation range was a guarantee of a certain volatility of the fuel. The distillation curve, therefore, was a measure of the homogeneity and of the volatility of the fuel. This latter could be limited, so that danger from vapour lock could be avoided. The Aéronautique française fixed a standard distillation curve for fuels.

The progress made with regard to anti-detonation and with the work on vapour lock and vapour tension has led to the adoption of the following specifications:

$$\text{AIR—3401 and AIR—3402, AIR—}\frac{3401}{1/B}$$

Fuels for Aero-engines

Specifications and General Characteristics

These fuels are of two types:

Type (1). **Aero Fuels 'A'**. Composed exclusively of petroleum spirits, which may not be mixed with an 'anti-knock', and of which the octane number is fixed at a minimum value. These fuels are colourless.

Type (2). **Aero Fuels 'B'**. Composed exclusively of petroleum spirit which may or may not be mixed with a permissible 'anti-knock' and of which the octane number is fixed. These fuels are colourless, except when they contain an 'anti-knock' which is toxic in character, when they are coloured blue by the addition of a specified material. The quantity of colour added should not exceed 0·4 g. per 100 litres.

Characteristics of the Fuels

(1) Density.

Determined at 15° C. by the usual balance method, or by pyknometer. The density should be lower than 0·780.

(2) Water Test.

Determined by using anhydrous copper sulphate. The result of this test should be negative.

(3) Sulphur Content.

Using the methods AIR 1085 (part AFNOR B. 6–14). Sulphur content by Grote's method. Corrosive sulphur, by copper dish. There should be no corrosive sulphur and the total sulphur content should not exceed 0·15%.

(4) Neutrality.

By the method AIR 1086. The fuel should be neutral (i.e. neither acid nor alkaline). Fuels for aircraft engines agree with the specifications fixed by the method AIR 3402. AIR 3402/1.

Fuels for Aircraft Engines

Specifications and Particular Characteristics

These fuels should be obtained by direct distillation and exclude all fuels produced by cracking and hydrogenation where the methods of production do not allow precise control of the quality of these latter.

(1) Distillation.

Method AIR 1085 (AFNOR B. 6–11—A.S.T.M. Distillation, Engler Distillation).

The volume to be noted at the following temperatures.

Temperature	*Limits for volume distilled*
75° C. . . .	10–20%
100° C. . . .	50% minimum
150° C. . . .	90% minimum

The end-point should be 180° C. or less.

The distillate should not be less than 96%.

The residue should be 2% or less by volume. It should be tested for neutrality according to Method AIR 1086.

(2) Vapour Pressure.

The method is AIR 1087 (Reid Bomb). The temperature to be 38±0·5° C.; the pressure should not exceed 0·5 kg. per sq. cm.

(3) Congealing-point or Freezing-point.

The method is AIR 1088. The temperature at which crystals appear should be −45° C. or less.

(4) Gum Content.

(*a*) **Existent Gum.** Method AIR 1085 (AFNOR B. 6–13). The weight of gum is obtained after evaporation of the spirit under standard conditions.

The quantity should be less than 6 mg. per 100 c.c. of spirit.

(*c*) **Potential Gum.** In the absence of a method of measuring potential gum content the method of AIR 1089 is used, i.e. determination of the per cent. content of ethylene type of hydrocarbons. The percentage expressed as amylene should be 2% or less.

(5) Octane Number.

Method AIR 1090. Modified C.F.R. method. The octane number for 'Aero Fuels A' should be a minimum of 70 while that for 'Aero Fuels B' should be a minimum of 87 with a tolerance of 4–2.

(6) 'Anti-knock' Content.

In 'Aero Fuels B' the addition of ethyl lead fluid should be such that the lead content is 0·8 c.c. of ethyl lead fluid per 1,000 c.c. of fuel.

In these methods the fuels have been placed in two categories, i.e. those which do not contain 'anti-knocks' and those which do contain such bodies. The following are the standard knock ratings for these fuels, as determined by the C.F.R. motor method, modified for aviation fuels (i.e. the modified motor method only differs from the normal method by the inlet temperature, this being 127° C. in the modified method and 149° C. in the normal method); for the first type an octane number of 70, and 85 for the second. The allowable tolerance is 2. These figures have been adopted as they apply to existing French engines. The density is limited to a maximum of 0·780, which allows up to 50% of benzene to be mixed with the fuel; this, together with the standard distillation range, eliminates heavy saturated products. There is an upper limit for the quantity of benzene that can be added, since the crystallization point of the fuel is fixed at a low figure.

The fuel should be neutral and should not have a total sulphur content higher than 0·15%, and it should not contain any corrosive sulphur.

The freezing-point of the fuel in view of its use at high altitudes is limited to −45° C., i.e. this is the temperature at which crystals appear.

The vapour pressure of the fuel must not exceed 0·5 kg. per sq. cm. as determined in the Reid bomb in order to avoid vapour lock. The A.S.T.M. distillation curve shows that the fuel is homogeneous and acceptable for the purpose for which it is used.

French specifications do not permit the use of cracked and hydrogenated fuels, and these notes are given for those products which are permissible. They give the properties which assure sufficient stability of the fuels, when determined by the appropriate methods.

The actual gum content is fixed at a maximum of 6 mg. per 100 c.c. and the ethylenic hydrocarbons present must not exceed 2% expressed as amylene.

Methods.

Most of the methods given here (e.g. A.S.T.M. distillation, Reid vapour pressure, C.F.R. motor method for octane number, &c.) are sufficiently well-known international methods. The method of determining the freezing-point, however, is a particular one of the French Air Ministry. It is given under the serial designation AIR 1088/1 as in the following: AIR 1088/1—Freezing-point, or Congealing Point.

1. **Rapid Method**. Twenty cubic centimetres of the fuel to be tested is placed in a closed test-tube in which is placed a thermometer reading to low temperatures.

This tube is then placed in a Dewar flask containing a refrigerant, e.g. solid carbon dioxide and acetone. The temperature is noted at which the crystals first appear; the tube is then allowed to warm up and the temperature again noted at which the crystals first disappear.

By repeated freezing and warming the exact crystallization temperature is obtained.

2. **Accurate Method.** The apparatus consists of a Dewar flask containing a refrigerant, which is at a temperature several degrees higher than the freezing-point of the fuel as determined approximately; a stopper is fitted to this flask through which passes a tube containing 30 c.c. of the fuel under test, in which is a low-range thermometer and a stirrer. A further tube containing acetone cooled by the addition of solid carbon dioxide is placed such that it is in contact with the fuel under test.

The temperature is slowly reduced until crystals appear. At this point the tube containing the freezing mixture is raised and the temperature of the fuel which is constantly agitated thus increases. The temperature at which the crystals disappear is noted.

SPECIAL ENGINE FUELS

By D. A. HOWES, D.Sc., M.Inst.P.T.
Anglo-Iranian Oil Company Ltd.

Introduction

THIS article deals with certain special engine fuels which are not separately dealt with elsewhere. These fuels are considered in the following order:

1. Recent aviation fuels.
    - (*a*) Iso-pentane.
    - (*b*) Iso-octane.
    - (*c*) Di-isopropyl ether.
    - (*d*) Safety aviation fuels.
2. Hydrocarbon fuels produced by the catalytic treatment of water gas, i.e. Synthol.
3. Tar-oil and creosote fuels for spark-ignition engines.
4. Alcohol fuels and racing fuels.
5. Gaseous fuels.

Recent Aviation Fuels

For a number of years there has been an incessant demand for aviation fuels of higher octane number, and although fuels of 87–92 octane number are now being regularly supplied in Europe and in America the demand still persists. Recent developments have made the production of 100 octane number fuels in large quantity a commercial proposition, but it is probable that, within a short time, fuels of 100–120 octane number will be available. The demand for such fuels is due to the greatly increased engine performance obtainable by their use, particularly with regard to take-off power, and power obtainable under full-throttle conditions at high supercharger boost pressures. Since 1930 the aviation fuels supplied in America have been as follows, the average octane numbers given being computed on a gallonage basis:

	U.S. Army Air Corps	*Three leading air lines*
1930 . .	70·6	73
1931 . .	77·7	73
1932 . .	82·2	73
1933 . .	87·3	78·9
1934 . .	90·2	80·4

Compared with fuels of 90 octane number those of 100 octane number give a 15–30% increased power output and specific fuel consumptions as low as 0·34 lb. per B.H.P.H.

(*a*) Iso-pentane.

Iso-pentane is present in the light fractions of nearly all crude petroleums and has an octane number, as determined by the C.F.R. Motor method, of *c.* 90. Its only disadvantages are its low boiling-point and high vapour pressure, but it is, of course, to be preferred to both normal and iso-butane in these two respects as shown in the following figures [48, 1936].

	Iso-pentane	*n-Butane*	*Iso-butane*
Octane number, C.F.R. Motor method	90	91	99
Boiling-point, ° C.	27·8	−0·6	−12
Sp. gr.	0·625	0·585	0·565
Reid vapour pressure, lb. per sq. in. at 100° F.	20·4	52·5	74

Iso-pentane is now being used to a large extent for incorporation in aviation fuels of low volatility such as iso-octane blends, and is especially valuable for this purpose because of its high anti-knock value. In blends containing about 2 c.c. per gal. of lead, iso-pentane has an anti-knock value 92–100% that of octane. Iso-pentane is not used in an undiluted state because of its low boiling-point and high vapour pressure, but it is an excellent blend stock. It is available in huge quantities and may be recovered from natural gasolines by simple but efficient fractionation.

(*b*) Iso-octane.

In 1934 announcements were made to the effect that iso-octane (2,2,4-trimethyl pentane), first discovered by Graham Edgar in 1927, and later used as a primary reference fuel in the determination of knock ratings, was about to be produced on a large scale for incorporation in aviation fuels. At the present time it is being produced in large quantities and has already demonstrated its great value as a component of fuels for high-output aero-engines. The methods by which iso-octane may be prepared are dealt with in detail elsewhere, and it suffices here to mention its properties and uses.

By definition of the terms of reference at present used for the expression of anti-knock value, iso-octane has an octane number of 100. This is, however, purely an arbitrary standard, and it is possible that with the introduction of new fuels of anti-knock values of this order a new scale or standard will have to be adopted. Whatever blends of aviation gasoline and iso-octane may be used in aviation, it is practically certain that tetra-ethyl lead will be used still further to increase their anti-knock value. Iso-octane blends have good lead response, and it is possible to produce fuels having octane numbers up to 110 with normal lead concentrations.

In February 1936 Klein presented details regarding work carried out by the Material Division of the U.S. Army [38, 1935]. Four fuels were tested on the basis of comparative performance with 92 octane number fuel to specification no. Y3557-G. These were:

1. 50% iso-octane+50% aviation gasoline+3 c.c. lead.
2. Same as 1, but containing 6 c.c. lead.
3. Reference fuel C 6+8·5 c.c. lead.
4. 37·5% iso-octane+37·5% high anti-knock fuel half composed of aromatics+25% pentane+1 c.c. lead.

Engine tests failed to reveal any substantial difference between 1 and 2, which differ only in lead content. In the case of No. 4 fuel, the iso-octane was used to increase the lead susceptibility of the aromatic fuel and the iso-pentane was added to correct distillation properties.

On the basis of tests in Wasp and Cyclone Aero-engines, Klein concluded that iso-octane blends were highly satisfactory.

On the other hand, Wood [66, 1936] has described tests in the water-cooled Rolls-Royce 'Kestrel' aero-engine in which a 95/96 octane number non-aromatic iso-octane blend was inferior from the detonation point of view to a 92 octane 30% aromatic fuel to DTD. 224 specification containing 7 c.c. lead. It would appear that iso-octane blends show to advantage in air-cooled engines, where the disadvantages of overheating attached to the aromatic fuels mitigate against their satisfactory use.

Fig. 1 shows the octane numbers of blends of iso-octane and isopropyl ether in the same aviation gasoline.

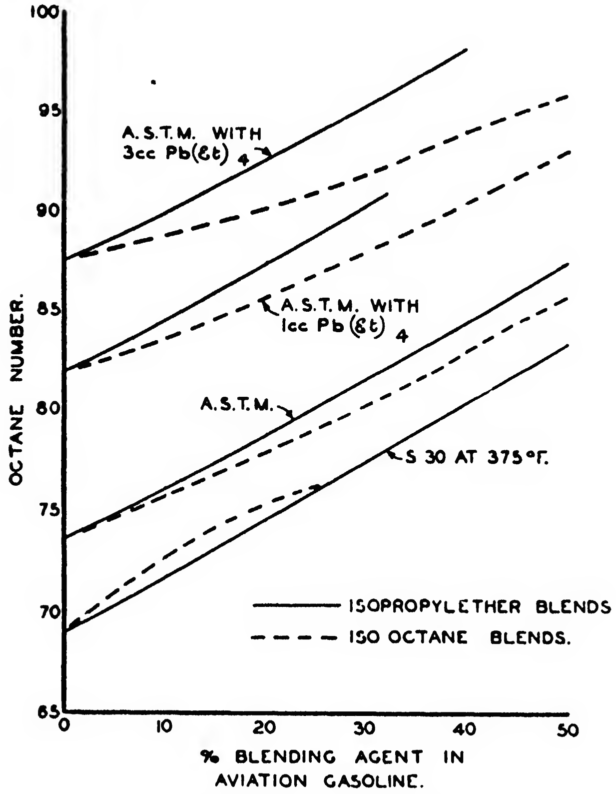


FIG. 1. Octane ratings of isopropyl ether and iso-octane in aviation gasoline.

(*c*) Di-isopropyl Ether.

Contrary to the behaviour of di-ethyl ether, which is a violent knock inducer, isopropyl ether, along with some other ethers, has been found to be possessed of good anti-knock properties [3, 1936]. The physical properties of this substance, together with corresponding values for benzene and pure iso-octane, are given in the following table. Despite its low boiling-point, the vapour pressure of isopropyl ether is below the maximum allowed in most aviation fuels and hence is entirely satisfactory in this respect. The freezing-point is also satisfactory. The latent heat is comparable with that of iso-octane, although lower than that of benzene, but the calorific value is lower than that of either hydrocarbon. This would normally result in a higher specific fuel consumption, but in practical blends the effect is counterbalanced by the ability to operate on leaner mixture strengths without developing excessive cylinder-head temperatures.

Unfortunately isopropyl ether is slightly soluble in water, a fact which gives all fuel blends containing it a definite 'water tolerance'. This is of considerable importance because nearly all fuels are stored in tanks containing a water bottom, and in the U.S. Army Air Corps water displacement storage systems are in use. Tests carried out by Buc and Aldrin [3, 1936] have shown that the solubility of water in a 60/40 aviation gasoline-isopropyl ether blend at 72° F. (22° C.) is much higher than in a corresponding benzole blend or in aviation gasoline alone—thus:

TABLE I

	Isopropyl ether	*Pure iso-octane*	*Benzene*
Boiling-point, ° C. at 760 mm.	67·8	99·4	79·4
Density, 20/4°	0·725	0·691	0·878
Refractive index at 20° C.	1·3680	1·3921	1·5014
Freezing-point, ° C.	−87	−108	+5
Viscosity, centipoises at 20° C.	0·322	0·543	0·647
Latent heat, B.Th.U. per lb.	123	130	170
Gross calorific value, B.Th.U. per lb.	16,900	20,580	17,650
Net calorific value, B.Th.U. per lb.	15,600	19,200	17,000
Net calorific value+latent heat, B.Th.U. per gal.	93,100	111,400	125,700
Reid vapour pressure, lb. per sq. in. at 100° F.	5·3	2·2	3·2

	Solubility of water, ml. per 100 ml. fuel at 72° F.
Aviation gasoline	0·007
„ +40% benzole	0·022
„ +40% isopropyl ether	0·055

Similarly, the amount of water which separates from a saturated fuel solution is greater in the case of an isopropyl ether blend than in the case of a benzole blend, as shown in the following figures, which refer to the amount of water in ml. per 100 ml. fuel separated on cooling a saturated solution at 70 to −20° F. (21 to −29° C.).

Aviation gasoline	0·0005
„ +40% benzole	0·003
„ +40% isopropyl ether	0·0055

With regard to storage stability, Buc and Aldrin [3, 1936] have stated that this is satisfactory in the presence of benzyl-amino-phenol gum inhibitor, and this is important as the ease with which isopropyl ether forms explosive peroxides in storage has recently been remarked upon.

A comparison between the properties of an isopropyl ether aviation spirit blend, an iso-octane blend, and the U.S. Army specification requirements for 100 octane number aviation spirits is given in Table II.

The anti-knock properties of di-isopropyl ether may be summarized as follows:

1. Blended in commercial aviation gasolines of 85–7 octane number, a fuel of 100 octane number (U.S. Army method) is possible with about 40% concentration of isopropyl ether without exceeding a tetra-ethyl lead concentration of 3 c.c. per U.S. gal.
2. The blending value of isopropyl ether is slightly superior to that of technical iso-octane in unleaded blends and also superior for any fixed amount of tetra-ethyl lead in corresponding blends.
3. When blended with 74–5 octane number aviation gasoline, and without exceeding 3 c.c. of lead per U.S. gal., an octane number of 101–2 is the maximum possible when using technical iso-octane as a blending agent, whereas isopropyl ether will give at least 105 octane number in concentrations of about 65% or over.
4. The amount of tetra-ethyl lead necessary to meet a given octane number is less for isopropyl ether than for technical iso-octane in blends containing the same percentage concentrations.

TABLE II

100 Octane Number Aviation Fuels

	U.S. Army specification 100 O.N. fuels	*Isopropyl ether aviation spirit blend*	*Iso-octane aviation spirit blend*
Octane number (U.S. Army method)	100	100	100
M.L. tetra-ethyl lead per U.S. gal.	3 max.	3	3
Copper dish corrosion test	must pass	passes	passes
Gum after accelerated, ageing test, mg. per 100 ml.	10 max.	9·8	5·0
Sulphur, % wt.	0·10 max.	0·02	0·02
Distillation test:			
Per cent. condensed at 150° F. (65·5° C.)	..	8·5	5·0
„ „ „ 158° F. (70·0° C.)	..	22·0	8·0
„ evaporated at 167° F. (75·0° C.)	10 min.	47·5	14·0
„ „ „ 212° F. (100° C.)	50 „	90·0	64·0
„ „ „ 275° F. (135·0° C.)	90 „	99·0	..
Sum of 10% and 50% evaporation points in ° F.	307 „	319	364
Per cent. residue	2 max.	1·0	1·0
Reid vapour pressure at 100° F.	7 lb. max.	6·0	6·0
Freezing-point	−76° F. (−54·4° C.) max.	below −148° F.	below −148° F.
Water tolerance:			
Ml. change in volume of 20 ml. water after shaking with 80 ml. gasoline at 75° F.	2 max.	nil	nil
Product of gross calorific value (B.Th.U. per lb.) and specific gravity	13,700	14,310	14,350
Specific gravity:			
Gross calorific value, B.Th.U. per lb.	..	19,360	20,820
Net „ „ „ „	..	17,890	19,410
„ „ „ +latent heat, B.Th.U. per lb.	..	18,120	19,550
B.Th.U. per gal. (U.S.)	..	109,400	114,500
Composition	not specified	40% isopropyl ether in aviation gasoline	45% iso-octane in aviation gasoline

The question of cruising range possible with various fuels naturally raises the question of the limitation of isopropyl ether blends due to their lower heat of combustion per gallon. Buc and Aldrin have stated, however, that this is counterbalanced by the fact that satisfactory engine operation can be obtained on such blends by working at mixture strengths leaner than usual with normal aviation fuels or with aviation fuels containing iso-octane. Also, the lower calorific value of isopropyl ether may be overcome by using blends of higher octane number than is possible with iso-octane.

Di-isopropyl ether may be produced from propylene (available in enormous quantities in cracked gases) via isopropyl alcohol.

With regard to the anti-knock value of other ethers, practically no information is available in the literature, although one statement has been made to the effect that di-tertiary butyl ether is rather more effective than di-isopropyl ether [37, 1936].

(*d*) 'Safety' Aviation Fuels.

Considerable attention has recently been given to aviation fuels for spark-ignition aero-engines having high flash-points—the so-called 'Safety' Aviation Fuels.

Perhaps the greatest argument in favour of such fuels for use in aircraft is the elimination of the fire risk that is ever present when normal fuels are employed. The elimination of this fire risk would do much to popularize aircraft and to make the public at large more air minded. Attempts to provide fuels of high flash-point suitable for modern aero-engines may be divided into two classes. In the first trials have been made with kerosines and white spirits containing tetra-ethyl lead in quantity sufficient to give the high octane numbers required. These trials have not been completely satisfactory, although the adoption of other carburetting arrangements may enable such fuels to be used with advantage. The most important safety aviation fuels are those produced by a special use of the high-pressure destructive hydrogenation process. In this the hydrogenation is applied to feed stocks such as the extracts obtained in the Edeleanu treatment of kerosines and gas oils, and the product obtained is distilled into two fractions. The bottom fraction comprises the 'safety' fuel and the overhead product a normal aviation fuel. The following example of such an operation has been given by Byrne, Gohr, and Haslam [5, 1932].

Feed stock

Sp. gr	0·90
Per cent. sulphur	0·89
Aniline-point	10° F. (−12° C.)
Initial boiling-point	175·5° C. (348° F.)
Final boiling-point	299° C. (570° F.)

Product	*Light aviation fuel*	*Safety fuel*
Yield on feed, %	29	55
Specific gravity	0·783	0·885
Flash-point (Abel)	..	107° F. (41·6° C.)
Colour. Saybolt	30	28
Doctor test	negative	negative
Corrosion test	passes	passes
Initial boiling-point	100° F. (37·8° C.)	309° F. (154° C.)
Final boiling-point	335° F. (168·4° C.)	411° F. (210·6° C.)
Octane number (S30 engine, 300° F. jacket temp.)	83	93

The satisfactory use of such fuels demands special carburetting arrangements because of their non-volatile character, but developments recently made in the application of solid injection indicate that this method is better able to make use of the valuable properties of such fuels. Conventional carburettors have many limitations and disadvantages—they demand a sufficiently high fuel volatility so that the fuel may be at least partly vaporized and carried by the air stream into the cylinders, and as a metering device, for both air and fuel, they leave much to be desired. Moreover, they limit the volumetric efficiencies of engines on which they are used because of pressure drop through their restrictions and actual mechanical load of carrying the fuel.

For some time the idea of using the mechanical system of injection, as used in the Diesel engine, has been receiving attention both in America and in England, and much experimental and development work along these lines has been carried out. Mechanical fuel pumps are used to inject the fuel into the engine cylinders, and the moment of injection is timed to take place at any convenient time between the beginning of the suction stroke and the end of the compression stroke. Generally better fuel economy and greater power is obtained by injecting after the closing of the inlet valve. By injecting in this way, the fuel is metered mechanically and is distributed in exact quantities directly to the cylinder for which it is intended, thus overcoming all the distribution problems of the conventional carburettor and induction system.

The advantages of this method of operation are numerous. Generally the optimum power output is increased from 10 to 20%, due to increased volumetric efficiency (due to absence of fuel and air preheat) and improved distribution. The engine becomes more responsive to variations in fuel supply because the fuel is handled mechanically and positively and the time lag of the carburettor is completely eliminated. Starting is also claimed to be improved because of the atomization obtained on injection. A further advantage, with particular regard to aviation conditions, is that freezing of the carburettor due to ice formation at high altitudes is completely eliminated.

Such a development is likely to play an important part in aircraft operation in the near future, especially in conjunction with fuels of high octane number, such as iso-octane blends—in addition to safety fuels.

Experimental work on the direct injection of fuel into spark-ignition engines has been carried out by Taylor and Williams [59, 1931–2]. The engine used was a standard C.F.R. unit coupled to a dynamometer and a Bosch cam-operated plunger type fuel pump driven through a planetary gear drive, which permitted easy adjustment of the injection timing. The injection valve was of special design, and its position with respect to the combustion chamber was such that the axis of the spray cone made an angle of 45° with the cylinder axis. A shrouded inlet valve was employed to give various types of turbulence. Tests were carried out on a normal aviation spirit, a safety aviation fuel of the above-mentioned characteristics, and a straight petroleum distillate (I.B.P. = 240° C. 80% distillate at 316° C.)—all of which were examined at a compression ratio of 5 to 1, at full throttle and at 1,000 r.p.m. With the aviation spirit it was found that the best performance was obtained when injection began simultaneously with the closing of the inlet valve, and under these conditions the power output increased by 5–7%, and the specific fuel consumption decreased by 6–11% as compared with a carburettor. The heavier fuels, surprisingly enough, had a wider permissible range of injection timings than the normal aviation spirit and could be injected at the low compression ratio of 4 to 1 as late as 110° after bottom centre, whereas the normal aviation spirit could not be injected later than 90° without misfiring. However, with injection later than bottom centre, a fair degree of directed turbulence was found essential to give proper distribution of the fuel through the combustion space and to assure homogeneity of the charge to obtain good combustion. The best performance was obtained on the safety fuel—this giving the highest B.M.E.P. and the lowest specific fuel consumption.

It is understood that the Pratt and Witney Aircraft Company of East Hartford, Connecticut, U.S.A., are actively interested in this new development, and announcements have been made to the effect that the British Government's Aeronautical Research Committee have pursued work on this subject beyond the stage of preliminary experiments and are continuing their investigations.

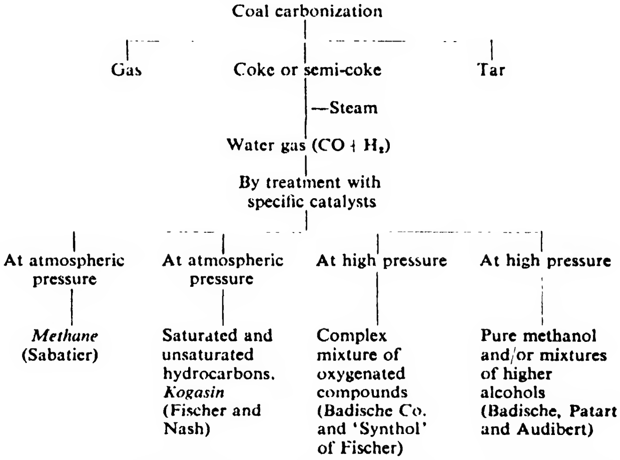
A short review of the possibilities of direct injection has been given by Ensor [16, 1935].

Hydrocarbon Fuels produced by the Catalytic Treatment of Water Gas

The production of liquid fuels from coal has been investigated for a considerable period and syntheses via coke and water gas have assumed commercial importance, particularly the high-pressure methanol and higher alcohol synthetic processes. These, and other developments, are shown diagrammatically in the following chart.

TABLE III

Synthesis from Coal via Coke and Water Gas



Sabatier [56] pointed out in 1905 that, as two of the valency directions of carbon monoxide (one of the two constituents of water gas, hydrogen being the other) are unsatisfied, the molecule will combine with oxygen, sulphur, and chlorine, and it should combine therefore with hydrogen to give formaldehyde and then methyl alcohol. The use of a nickel catalyst gave methane only.

It appears that up to the year 1913 the formation of methane, carbon dioxide, and water were the only established reactions when carbon monoxide and hydrogen were passed over a catalyst. In 1913 appeared a patent of the Badische Company (G.P. 293,787 (8 March 1913), with additions 295,202 (31 May 1914) and 295,203 (23 June 1914), and corresponding B.P. 20,488 of 1915) describing the formation of liquid hydrocarbon and oxygenated compounds by passing carbon monoxide together with an excess of hydrogen over a catalyst. Pressure was employed and temperatures higher than 250° C. The catalyst mentioned was alkali and zinc carbonate on pumice. Attempts to verify the claims of these patents were made by Fischer and Tropsch with no success. However, the use of a modified catalyst led to the desired results, and the iron-alkali catalyst developed by these investigators gave from water gas at about 400° C. and several atmospheres pressure a product, called 'Synthol', which compressed a mixture of aliphatic alcohols, aldehydes, ketones, acids, esters, and hydrocarbons [26, 1923–5]. Subsequent to 1913 numerous patents were taken out by the Badische Company relating to the synthesis of liquids—particularly methanol—from water gas, and a great variety of oxides and metals have been specified as suitable catalysts.

In France similar investigations were carried out by Patart [50, 1925] and Audibert [1, 1925]. Patart was mainly interested in methanol production and demonstrated that at 400–420° C. and 150–250 atm. pressure methanol was produced from water gas using zinc oxide as catalyst. Audibert investigated the catalytic activity of various sub-oxides such as CrO, U_2O_3, &c., and found that methanol was produced in a pure condition at 225–300° C. At temperatures higher than 300° C. other organic compounds, water, and methane appeared in the products. The addition of a strong base to one of the active sub-oxides induced the formation of a mixture of compounds which formed an aqueous and an oily layer similar to the mixture obtained by Fischer and Tropsch. Comparatively small yields were obtained by the use of the oxides alone.

In 1926 Fischer and Tropsch [2, 1926] described the production of petroleum-like hydrocarbon materials from water gas by atmospheric-pressure operation. The catalysts employed were the metals, or partly reduced oxides, of group 8 of the Periodic Classification, and it was considered expedient to make additions to prevent sintering and to accelerate carbide formation (carbides being considered by Fischer and Tropsch to be the intermediate compounds formed in this reaction). Iron and cobalt appeared to be satisfactory catalyst materials. The passage of hydrogen and carbon monoxide over iron-zinc oxide gave a mixture of methane and homologues, but the use of cobalt and chromium oxides at 270° C. led to the formation of liquid and solid, as well as gaseous, hydrocarbons. These observations were confirmed by Elvins and Nash [15, 1926], who obtained in addition to hydrocarbons also oxygenated substances soluble in water when using catalysts comprising reduced copper, cobalt, and manganese oxides. The production of olefine hydrocarbons in the liquid products was also observed.

Tests on various catalysts comprising cobalt metal used in conjunction with copper and other metal oxides were described by Erdely and Nash in 1928 [21], who reached the following conclusions:

1. At a temperature of 285° C. and atmospheric pressure, using a gas containing equal volumes of carbon monoxide and hydrogen, a cobalt-copper-zinc oxide catalyst was the most suitable. Nearly as satisfactory was a cobalt-copper-alumina catalyst, but this formed less oil and more water. The oil yield was highest with a non-promoted cobalt-copper catalyst, but the activity of this catalyst rapidly deteriorated.
2. The best temperature for the formation of liquid hydrocarbons was found in the case of cobalt-copper-alumina catalyst to lie between 280 and 290° C. Above this chiefly carbon dioxide and methane were formed. Below 230° C. no reaction could be observed.
3. An excess of hydrogen in the original gas mixture increased the formation of water, while an excess of carbon monoxide rapidly lowered the activity of the catalyst.
4. The optimum space velocity in the case of a cobalt-copper-zinc oxide catalyst was about 120 vol. of gas per hour per unit volume of catalyst (measured at N.T.P.).

The work of Fischer has continued to the present time, and the process for the production of liquid hydrocarbon fuels from water gas is now almost universally known as the *Fischer Process*—the liquid products obtained being known as *Kogasin.* The gas mixture usually employed is $CO:H_2 = 1:2$, and this must be free of H_2S and not contain organic sulphur compounds to an extent greater than 0·2 g. per 100 cu. m. Of the catalytic materials available (normally used on a Kieselguhr support) cobalt-base catalysts appear to be favoured, giving a yield of 130 g. of liquid hydrocarbons per 1 cu. m. of gas treated. Modified nickel-base catalysts have been investigated, in the production of which an aluminium or silicon alloy is treated with sodium hydroxide solution to give a skeleton of the insoluble constituents of the alloy [25, 1934].

The reaction is strongly exothermic, as shown by the following equation given by Fischer:

$$CO+2H_2 = (CH_2)_x+H_2O+48 \text{ kg.-cal.}$$

The products from the reaction comprise hydrocarbon, oil, and water in proportions varying from 1:1 to 1:2 together with small quantities of gaseous hydrocarbons and a hard wax which becomes deposited on the catalyst. Small quantities, i.e. traces, of oxygenated compounds are present in the liquid products, and recently a number of fatty acids have been isolated [40, 1935].

The composition of the hydrocarbon products obtained are illustrated by the following figures referring to an initial gas mixture containing 20% CO and 58% H_2 and a cobalt-base catalyst [23, 1925].

Component	*Boiling range, ° C.*	*% by weight*	*Olefine content, % vol.*
Low-boiling fraction . .	below 30	4	50
Benzine	30–200	62	30
Heavy oil	above 200	23	10
Solid paraffin from the oil .	m.p. 50	7	. .
Hard paraffin from catalyst .	m.p. 70–80	4	. .

Usually the olefine content of the liquid products is lower when a nickel catalyst is used, or when an initial gas containing a greater concentration of hydrogen is employed—as shown in the following figures given by Fischer.

Basic metal in catalyst	*Volume % of olefines in benzine from gas mixtures of composition*		
	$CO:H_2 = 1:1$	$CO:H_2 = 1:2$	$CO:H_2 = 1:3$
Cobalt . .	55	35	12
Nickel . .	35	16	5

With regard to the distribution of olefines in the product, in general the olefine content falls with rise in boiling-point. Thus in the case of a product obtained from a gas of the composition $CO:H_2 = 1:2$, the following figures have been quoted.

	Volume %	*Olefine content, vol. %*
Original . .	100	26
50–100° C. . .	22·5	39
100–150° C. . .	20	27
150–200° C. . .	19·5	18
200–250° C. . .	13	11

TABLE V

Specifications for Tar-oil Fuels for Spark-ignition Engines

Specification	*Belfast Corporation Gas Department*	*London General Omnibus Company*	*Gas Light and Coke Company*	*Newcastle-upon-Tyne and Gateshead Gas Company*
Composition and description	90% light creosote oil (washed and redistilled) 10% 90/190 water-white solvent naphtha	Redistilled creosote with sufficient benzole to prevent separation of naphthalene at any low temperature likely to be experienced. The mixture to be free of water and adventitious matter	Redistilled creosote mixed with sufficient benzole to prevent separation at any temp. likely to be experienced. The mixture to be free of water and adventitious matter	..
Specific gravity	0·951	Not below 0·935 at 15·5° C.	0·935–0·953 at 60° F.	0·922 at 15·5° C.
Tar acids	15%	Not to exceed 12% (approx.)	4·5–8·5%	4%
Carbon residue	0·34%*	Not to exceed 0·1%	Not to exceed 0·1%	..
Ash	0·04%	..	..	..
Flash-point	129° F.	..	70° F. max.	Below 73° F.
Water	nil	Not above 0·1%	Not above 0·2%	..
Distillation test	I.B.P. 148° C.†			
	10% at 180° C.	..	5% at 135–160° C.	10% at 150° C.
	20% ,, 189° C.	..	10% at 150–175° C.	20% at 165° C.
	30% ,, 198° C.	..	50% at 200–210° C.	50% at 190° C.
	40% ,, 206° C.	..	90% at 230–250° C.	90% at 225° C.
	50% ,, 213° C.	..	F.B.P. 225–265° C.	F.B.P. 270° C.
	60% ,, 221° C.	..	..	..
	70% ,, 230° C.	..	..	..
	80% ,, 244° C.	..	..	..
	90% ,, 273° C.	..	..	..
Cold test	Pour-point not above 10° F.—no appreciable formation of crystals at 0° F.	..	No deposit at 40° F. (summer) or 25° F. (winter). Viscosity 27–8 sec. Redwood at 100° F.	..

* Later reduced to 0·03%. † Average figures only.

tar oil to keep the naphthalene in solution at low temperatures. The reason for a retention of a portion of the tar acids is partly their solvent power for naphthalene. A fuel of very low tar acid content is possible if larger amounts of benzole or naphtha are present or if the creosote is derived from certain types of vertical retort tar, and in some cases the tar acid content has been reduced to as little as 1–2%. More refined methods of production have been used by some suppliers. In some cases naphthalene has been removed by systematic redistillation several times, and in others careful filtration and settling has been employed to ensure cleanliness. In another case, namely one in which a product containing only 0·5% of tar acids was made, naphthalene was removed from the washed creosote by crystallization and sulphuric acid and soda treatment applied prior to final redistillation.

The yield of coal-tar oils to specification quality is limited and the cost is much greater than if a straight tar distillate could be employed, rising to as high as 7*d.* to 8*d.* per gallon in England. Even so, some consumers claimed much reduced running costs as against gasoline.

The quantity of such fuel available in England without encroaching upon other markets has been estimated at 7% of the whole country's gasoline consumption, but, due to the present demand for creosote for hydrogenation, this figure has recently decreased considerably.

Types of Vehicles on which Tar-oil Fuels have been employed and the Engine Alterations required.

In view of the lack of volatility of tar-oil fuels, carburation is much more difficult than in the case of gasolines. It is therefore necessary to heat the induction system quite considerably, and this is effected by use of heat derived from the exhaust gases. Sufficient heat must be applied to give fuel vaporization and to ensure that condensation of fuel cannot occur in the induction pipe and so adversely affect throttle response and fuel distribution. Such heating of the fuel charge necessarily causes a considerable loss in volumetric efficiency and power output. Due to the fact that tar-oil fuels have high final boiling-points, considerable crankcase dilution and contamination occurs, and, to prevent this as much as possible, cooling-water temperatures should be maintained at as high a temperature as is convenient—namely above 80° C.

Various carburation arrangements have been developed for the use of such non-volatile fuels, among which the *Solex Bi-fuel System* is one of the most important, and by far the most widely used. This was developed in connexion with the pioneering work carried out in Belfast in 1929 and comprises a large carburettor for use on the tar-oil fuel and a small carburettor for use on gasoline.

In the A.E.C.-Solex system, the Solex principle is modified by the incorporation of thermostatic control which automatically changes over from one fuel to the other according to the temperature of the engine.

With regard to other engine modifications necessary for operation on tar-oil fuels, in many cases the compression ratio has been increased to take advantage of the increased anti-knock value of the fuel. This often entails heavy initial costs in stiffening up the crankshaft and increasing the bearing diameters in order to accommodate the increased stresses involved.

Behaviour of Tar-oil Fuels.

Tar-oil fuels possess a number of disadvantages which have caused a number of users to decide that the use of such fuels is definitely impracticable.

Exhaust Gases.

These have usually a pronounced odour of creosote, but are clear under normal running conditions. There is generally evidence of smoke during the change over from petrol to tar oil, during acceleration, and also during gear changing. These objections have led to the discontinuance of the use of such fuels in London by London Transport and in Manchester by the Corporation Transport Department. One good feature is shown by the exhaust gases from engines running on tar-oil fuel—namely, the comparative absence of carbon monoxide.

Lubrication.

Much sludge formation occurs in engines running on tar-oil fuels and using normal lubricating oils, although with castor oil lubricants this trouble is reduced.

Mechanical Troubles.

These take the form of abnormal wear, overheating, gumming of valves, and sparking-plugs. With regard to the first item, the following individual instances of abnormal wear have been mentioned:

(*a*) Inlet-valve stems.
(*b*) Crankshaft main bearings, bottom end, and cylinder walls.
(*c*) Cylinder.
(*d*) Big-end bearings.
(*e*) Valves and valve seatings.

Figures given by the Belfast Omnibus Company are as follows:

	Approximate increased wear relative to petrol, %
Cylinder	50
Timing chain	50
Timing gear	50
Gudgeon pin	50
Big-end bearing	10
Journals	10

Furthermore, tar-oil fuels have a very bad corrosive effect on all brass and copper fittings.

The general concensus of opinion appears to be that the use of tar-oil fuels causes increased engine maintenance costs.

General Conclusions on the Use of Tar-oil Fuels in Spark-ignition Engines

The attempts made in Great Britain to popularize the use of the coal-tar oil fuels described has, in large measure, failed. The Belfast Omnibus Company, after using 72,000 gal. of the fuel in 28 omnibuses over a period of nearly 2 years, have reached the conclusion that their experience is unfavourable and have discontinued the use of the fuel. The London General Omnibus Company quite early in their work formed the opinion that the use of tar oil in their fleet is impracticable. In the long run nearly all users find that the disadvantages outweigh the advantages.

Alcohol Fuels and Racing Fuels

Alcohols are used as internal-combustion engine fuels in two main fields.

1. As constituents of normal marketed motor fuels for use in motor vehicles.
2. As ingredients (sometimes major ingredients) in special fuels for high-duty engines used in racing and sports events.

In the former case the ever-increasing use of alcohols is brought about mainly by compulsory decrees rather than by any particular fuel value of the alcohols, whereas in the latter case these substances have properties which give them marked advantages over normal hydrocarbon fuels and are thus in good demand without the help of compulsory measures. The use of alcohols as constituents of normal fuels is rapidly gaining enormous proportions in Europe due to the extreme nationalist tendencies prevailing and due to the desire of each individual country to render itself as independent as possible of foreign oil supplies and to encourage its domestic agricultural industries. The following European countries enforce the admixture of domestic alcohol with imported motor fuels: Spain, Bulgaria, Italy, Latvia, Hungary, Czechoslovakia, Sweden, France, Germany, Yugoslavia, and Lithuania. As far as is known as present, Denmark, Greece, Holland, Portugal, Norway, Rumania, and Russia have not made similar restrictions.

In Ireland the Free State Government has enforced the admixture of 10% ethyl alcohol with imported motor spirit, while the use of alcohol in this way has received considerable support in the Union of South Africa, British India, Australia, and certain South American countries. In the United States of America, agricultural interests have unsuccessfully pressed for similar legislation despite the vast domestic petroleum resources, but plants for the production of ethyl alcohol from grain are being erected to determine costs of production, &c.

With regard to racing fuels, the total consumption of such fuels is naturally very small and does not appear likely to increase to any appreciable extent. Methanol and ethanol are often major constituents of such fuels.

Alcohols used as Motor-fuel Constituents.

Methanol and ethanol are the only alcohols used to any appreciable extent in motor fuels. The former is mainly produced by high-pressure catalytic synthesis from water gas by processes described in another article, while the bulk of the ethanol used in this way is made by fermentation processes applied to molasses and cereals. The quantity of synthetic ethyl alcohol used as motor fuel is small, but is likely to assume important proportions at an early date. The higher alcohols have not yet received serious study from this viewpoint, despite their many advantages over methanol and ethanol. Such advantages include higher calorific value and a reduced tendency to separate from solution in gasoline on the addition of small amounts of water, and it is thus evident that the higher alcohols, e.g. propanols and butanols, possess attractive properties. Their relatively high cost prevents their adoption as motor-fuel constituents at present, but the rapid development of synthetic processes may alter the present state of affairs. It may be mentioned, however, that the most abundant raw materials for the synthesis of these materials—namely propylenes and butylenes which are available in cracked petroleum gases—have now found a much more profitable outlet in the form of polymer gasolines of high anti-knock value, and it appears that the utilization of such substances for the production of alcohols on a large scale has, as a result, been deferred for a considerable time.

Methods Employed for the Production of Motor-fuel Alcohols.

Methanol. Full details concerning the high-pressure synthesis of methanol from water gas are given in the article by D. A. Howes devoted to this subject.

Methanol is also produced by wood distillation, but this has rapidly declined in recent years due to the advent of the cheaper synthetic process and at the present time is of minor importance. The process need not be considered as a means of producing methanol at a sufficiently low cost for use as fuel. The rapid decline of the wood distillation has also been hastened by the development of synthetic processes for the production of acetic acid.

The Production of Alcohols by Fermentation Processes.

The fermentation process for the manufacture of ethyl alcohol has been practised for many years. The raw materials are vegetable matter containing either sugar, starch (which has to be converted into sugar as a preliminary to fermentation), or cellulosic materials, the cellulose being converted by chemical treatment into fermentable sugars. In the manufacture of alcohol for potable purposes, of which the requirements are comparatively small, as compared with those for a liquid fuel, and for which a higher price is obtainable, cereal grains, such as barley and rye, are employed, but in the production of power alcohol, molasses, maize, sugar beet, and potatoes are more suitable raw materials. In the British Dominions cassava, Nipah palm juice, sweet potatoes, grasses, straws, and waste vegetable materials have also been considered in this direction. Nathan [47, 1928] has shown that for lack of acreage irrespective of all other considerations, the production of any but an infinitesimal quantity of alcohol for fuel purposes would be an impossibility in Great Britain. This is indicated in the following figures:

TABLE VI

Material	Area, acres	Yield per acre, tons	Total produce, tons	Alcohol: Gal. per ton raw material	Alcohol: Gal. per acre	Approximate requirements for 1,000,000,000 gal.: Produce, millions of tons	Approximate requirements for 1,000,000,000 gal.: Area in millions of acres
Potatoes	1,256,000	5·6	7,049,000	20	112	50	9
Mangolds	473,000	18·8	8,922,000	8	150	125	7
Sugar beet	222,500	7·7	1,450,000	22	170	45·5	6
Jerusalem artichokes	negligible	11·0	negligible	18	198	56	5

In the case of Great Britain, the only raw materials that could be grown for the production of ethyl alcohol for power purposes (apart from wheat and grain which are out of the question) are potatoes, mangolds, sugar beet, and Jerusalem artichokes, but the cost of the alcohol produced from these materials is very high.

In Germany the potato has for many years been the main source of industrial alcohol, potato growing being inaugurated more than a century ago in order to improve the sandy soils of east Germany, where the conditions of soil and climate were so unfavourable that without some such encouragement the country would have been in serious danger of depopulation.

In 1922 Monier-Williams [44, 1922] summed up English conditions, as far as the production of ethyl alcohol from potatoes was concerned, by stating that such a development 'would, undoubtedly, demand heavy State subvention and would not . . . be commercially practicable'.

The commercial production of alcohol from beet has been practised for many years in France (and in Europe, generally), and a large proportion of the industrial alcohol now produced in that country is manufactured from these roots. In Great Britain subsidies are given to sugar-beet production as an assistance to agriculture.

Details regarding the fermentation process for the production of ethyl alcohol may be found in other publications. The production of industrial alcohol from molasses at the Dagenham works of Solvent Products, Limited, has been described [35, 1928].

The production of ethyl alcohol from potatoes in Europe has been fully described by Williams [65, 1933]. After cooling the tubers are steamed under a pressure of 2–3 atm. for 1–2 hr. in order to gelatinize the starch. The resulting pulp is cooled to about 50° C., an equal volume of water added, the temperature raised to 40° C., and 10% malt added. The mixture is allowed to stand for 10–15 min. while the starch is converted to dextrin. The temperature is then gradually raised to 55° C., when the dextrin is converted to maltose, which in turn is partially transformed into dextrose. The mash is subsequently diluted with hot water at 80° C. to prevent the growth of bacteria, and the bulk of the solid matter is separated by centrifuging. Fermentation is begun at a temperature of 18° C., but the temperature rises soon after the addition of the yeast and must be held at about 28° C. by the circulation of cold water. The fermentation process occupies 3–4 days, and the yield obtained commercially is *c.* 50% of the starch content of the potatoes. The alcohol content of the wash may reach 9–10% as compared with about 4% in wash from sugar molasses. It is possible to produce 96–7% ethyl alcohol from the wash in one operation by the use of modern distillation plant. A certain amount (usually about 1% of the original starch content) of a low-boiling mixture—chiefly aldehydes—is obtained on primary distillation, and this, being unsuitable as a motor-fuel component, is rejected. Similarly, a small yield of fusel oil is also rejected.

Synthetic Processes for the Production of Alcohols.

The aliphatic alcohols, with the exception of methanol, may be produced by synthetic processes applied to olefines —the most convenient source of which is cracked gas. Two methods have been investigated, (*a*) the sulphuric acid process, and (*b*) the direct hydration process.

The production of ethanol and higher alcohols from cracked gases is described elsewhere, in the articles by R. Taylor ('Catalytic Production of Ethyl Alcohol from Ethylene') and B. T. Brooks ('Alcohols and Related Products from Petroleum Olefines').

Properties of Methanol and Ethyl Alcohol.

The physical properties of the lower alcohols and data concerning their aqueous solutions are detailed in Tables VII, VIII, and IX.

Solubility relationships with petroleum spirits and data concerning the use of blending agents are given in a separate article.

TABLE VII

Physical Properties of Methanol and Ethyl Alcohol

	Methanol	Ethyl alcohol
1. Ultimate composition:		
Carbon, % weight	37·5	52·1
Hydrogen, „	12·5	13·1
Oxygen, „	50·0	34·8
2. Boiling-point at 760 mm. Hg	64·7° C.	78·32° C.
3. Specific gravity at 15·5° C.	0·7965	0·794
4. Vapour pressure, mm. Hg:		
−10° C.	15·6	5·6
0° C.	29·65	12·2
10° C.	53·85	23·6
20° C.	93·95	43·9

TABLE VII (*cont.*)

	Methanol	*Ethyl alcohol*
4. Vapour pressure, mm. Hg:		
30° C.	157·0	78·8
40° C.	255·3	133·3
50° C.	405·5	222·2
60° C.	619·4	352·7
70° C.	929·0	542·5
5. Absolute viscosity, centipoises		
0° C.	0·808	1·77
10° C.	0·690	1·45
20° C.	0·593	1·19
30° C.	0·515	0·989
40° C.	0·449	0·827
50° C.	0·395	0·697
60° C.	0·349	0·591
6. Specific heat in liquid state, cal. 15°/g. per ° C.:		
0° C.	0·5665	0·5355
20° C.	0·600	. .
25° C.	. .	0·5810
40° C.	0·6165	0·6525
7. Latent heat of vaporization at the boiling-point:		
Joules per g.	1,100	885
Calories per g.	263	204·5
B.Th.U. per lb.	473	. .
8. Calorific value:		
Gross. C.H.U. per lb. . .	5,535	7,122
C.H.U. per gal. at 15° C. .	42,470	56,540
B.Th.U. per lb. . . .	9,605	12,820
Net. C.H.U. per lb. . .	4,730	6,491
C.H.U. per gal. at 15° C. .	37,650	51,530
B.Th.U. per lb. . . .	8,515	11,690
9. Theoretical air requirements for complete combustion:		
Pounds of air per lb. of fuel .	6·53	9·09
Pounds of air per gal. of fuel .	62·0	72·35
10. Explosive limits in air at 760 mm. pressure (% by volume) .	7·05–36·5	3·56–18·0
11. Volume of explosive mixture per g. molecule of fuel . . .	184 litres	346 litres
12. Volume ratio on combustion .	1·061	1·064
13. Flash-point in air, ° C. (approximate values only) . . .	−1–11° C.	11–14° C.

TABLE VIII

Specific gravities at 15° C./15° C. of Mixtures of Methyl Alcohol and Water and the Corresponding Percentages (by volume) of Methyl Alcohol

(Compiled from the table published in U.S. Bureau of Standards Circular no. 19, 1911)

% *methanol by volume*	*Specific gravity, 15°/15° C.*	% *methanol by volume*	*Specific gravity, 15°/15° C.*	% *methanol by volume*	*Specific gravity, 15°/15° C.*
0	1·0000	21	0·97295	42	0·94593
1	0·99851	22	0·97177	43	0·94443
2	0·99703	23	0·97058	44	0·94291
3	0·99560	24	0·96939	45	0·94136
4	0·99422	25	0·96820	46	0·93979
5	0·99283	26	0·96700	47	0·93820
6	0·99146	27	0·96580	48	0·93657
7	0·99011	28	0·96459	49	0·93493
8	0·98877	29	0·96338	50	0·93326
9	0·98746	30	0·96216	51	0·93155
10	0·98621	31	0·96091	52	0·92982
11	0·98496	32	0·95966	53	0·92806
12	0·98370	33	0·95838	54	0·92626
13	0·98247	34	0·95708	55	0·92443
14	0·98125	35	0·95576	56	0·92256
15	0·98003	36	0·95443	57	0·92067
16	0·97884	37	0·95308	58	0·91877
17	0·97766	38	0·95170	59	0·91682
18	0·97648	39	0·95029	60	0·91483
19	0·97530	40	0·94886	61	0·91282
20	0·97413	41	0·94741	62	0·91079

TABLE VIII (*cont.*)

% *methanol by volume*	*Specific gravity, 15°/15° C.*	% *methanol by volume*	*Specific gravity, 15°/15° C.*	% *methanol by volume*	*Specific gravity, 15°/15° C.*
63	0·90873	76	0·87836	89	0·83971
64	0·90663	77	0·87578	90	0·83623
65	0·90450	78	0·87312	91	0·83269
66	0·90234	79	0·87040	92	0·82907
67	0·90014	80	0·86760	93	0·82538
68	0·89790	81	0·86474	94	0·82163
69	0·89561	82	0·86180	95	0·81772
70	0·89327	83	0·85883	96	0·81363
71	0·89088	84	0·85582	97	0·80942
72	0·88844	85	0·85276	98	0·80514
73	0·88596	86	0·84967	99	0·80082
74	0·88346	87	0·84646	100	0·79647
75	0·88092	88	0·84314		

TABLE IX

Density and Percentage of Ethyl Alcohol by Volume and Percentage by Weight at 15·56° C. (Tralles)

Water = 0·991

Percentage of alcohol by volume	*Percentage of alcohol by weight*	*Density at 15·56° C.*	*Percentage of alcohol by volume*	*Percentage of alcohol by weight*	*Density at 15·56° C.*
0	0·00	0·9991	51	43·47	0·9315
1	0·80	0·9976	52	44·42	0·9295
2	1·60	0·9961	53	45·36	0·9275
3	2·40	0·9947	54	46·32	0·9254
4	3·20	0·9933	55	47·29	0·9234
5	4·00	0·9919	56	48·26	0·9213
6	4·81	0·9906	57	49·26	0·9192
7	5·62	0·9893	58	50·21	0·9170
8	6·43	0·9881	59	51·20	0·9148
9	7·24	0·9869	60	52·20	0·9126
10	8·05	0·9857	61	53·20	0·9104
11	8·87	0·9845	62	54·21	0·9082
12	9·69	0·9834	63	55·21	0·9059
13	10·51	0·9823	64	56·22	0·9036
14	11·33	0·9812	65	57·24	0·9013
15	12·15	0·9802	66	58·27	0·8989
16	12·98	0·9791	67	59·32	0·8965
17	13·80	0·9781	68	60·38	0·8941
18	14·63	0·9771	69	61·42	0·8917
19	15·46	0·9761	70	62·50	0·8892
20	16·28	0·9751	71	63·58	0·8867
21	17·11	0·9741	72	64·66	0·8842
22	17·95	0·9731	73	65·74	0·8817
23	18·78	0·9720	74	66·83	0·8791
24	19·62	0·9710	75	67·93	0·8765
25	20·46	0·9700	76	69·05	0·8739
26	21·30	0·9689	77	70·18	0·8712
27	22·14	0·9679	78	71·31	0·8685
28	22·99	0·9668	79	72·45	0·8658
29	23·84	0·9657	80	73·59	0·8631
30	24 69	0·9646	81	74·74	0·8603
31	25·55	0·9634	82	75·91	0·8575
32	26·41	0·9622	83	77·09	0·8547
33	27·27	0·9609	84	78·29	0·8518
34	28·13	0·9596	85	79·50	0·8488
35	28·99	0·9583	86	80·71	0·8458
36	29·86	0·9570	87	81·94	0·8428
37	30·74	0·9556	88	83·19	0·8397
38	31·62	0·9541	89	84·46	0·8365
39	32·50	0·9526	90	85·75	0·8332
40	33·39	0·9510	91	87·09	0·8299
41	34·28	0·9494	92	88·37	0·8265
42	34·18	0·9478	93	89·71	0·8230
43	36·08	0·9461	94	91·07	0·8194
44	36·99	0·9444	95	92·46	0·8157
45	37·90	0·9427	96	93·89	0·8118
46	38·82	0·9409	97	95·34	0·8077
47	39·74	0·9391	98	96·84	0·8034
48	40·66	0·9373	99	98·39	0·7988
49	41·59	0·9354	100	100·00	0·7939
50	42·52	0·9335			

Anti-knock Value of the Lower Alcohols.

Until a few years ago, the prevalent opinion with regard to methanol was that this substance is not capable of withstanding high compression ratios and that it possesses strong pre-ignition tendencies. This opinion is not shared by recent investigators, who have successfully applied methanol as a fuel for automobile and aircraft engines of the high-duty racing type. Howes [33, 1933] has described tests made on engines of many different types, from air-cooled motor-cycle engines to supercharged eight-cylinder racing-car engines, varying in compression ratio from 6·0 to 15·0 and in which no pre-ignition or knocking was observed when due care was taken to ensure adequate cooling. Further experiments on supercharged engines showed that methanol could be employed satisfactorily at static compression ratios up to 8·5 together with supercharger boost pressures up to 18 lb. per sq. in. gauge. In unsupercharged engines, compressions of over 15 to 1 have been used with satisfaction.

It would appear, then, that methanol is a valuable anti-knock fuel, and it is claimed that when mixed with gasoline it has an anti-knock value 1·8 to 2·0 times that of benzole, i.e. the addition of 10% of methanol to a gasoline increases the knock rating of the latter to the same extent as the addition of 18–20% of benzole. The results of tests carried out in an Armstrong-Whitworth variable compression engine and in an Ethyl Gasoline S. 30 engine are given in the following table:

TABLE X

Summarized results. Anti-knock value of Methanol

A. *Armstrong-Whitworth Variable Compression Engine.* 750 r.p.m. Jacket temperature, 50° C. Air-inlet temperature, 50° C. Spark advance, 12° B.T.D.C.

	H.U.C.R.	*Benzole equivalent of blend*	*Benzole equivalent of methanol*
Hydrogenated petrol .	6·85	. .	. .
,, +5% methanol .	7·15	10·0	2·0
,, +10% methanol	7·6	20·0	2·0
,, +12·5% methanol	8·05	25·1	2·0
,, +15% methanol	9·0	30·0	2·0

B. *Ethyl Gasoline S. 30 Engine.* Jacket temperature 150° C.

	Octane number	*C.c. Pb (Et) per U.S. gallon*	*% benzole*	*Benzole equivalent of methanol*
Reference fuel A2				
+30% benzole .	66·5	0·0	30	. .
+ 5% methanol	73·0	3·0	40	2·0
+10% methanol	80·8	over 10·0	49·5	1·95
+15% methanol	91·0	. .	59·6	1·93
+20% methanol	. .	. .	68·0	1·9

With regard to ethyl alcohol, the anti-knock value of this material has been recognized for some years and has not been disputed. In 1926 Ross and Ormandy [54] published figures which showed that 10% of ethyl alcohol had approximately the same effect in increasing the knock rating of a gasoline to which it was added as 20% of benzole. In 1924 Ricardo [53] found that ethyl alcohol had a H.U.C.R. above 7·5 to 1 and did not give any pre-ignition except after prolonged runs at engine speeds of 1,675 r.p.m. Recently published work support the previous findings of Ross and Ormandy.

With regard to the anti-knock value of the higher alcohols, the only available information is that published by Kuhring [41, 1934] with respect to isopropyl alcohol. This investigator gives the following figures for the octane numbers of alcohol blends in a straight-run gasoline determined in a S. 30 engine running at 900 r.p.m. and 345° F. jacket temperature.

	Octane number
Straight-run gasoline .	66·4
+10% isopropyl alcohol	71·0
+20% ,, ,,	75·75
+30% ,, ,,	79
+10% ethyl alcohol	74
+20% ,, ,,	79
+30% ,, ,,	83·5

Thus, under these conditions, isopropyl alcohol is definitely of lower anti-knock value than ethyl alcohol, 30% of isopropyl alcohol being equivalent to 20% ethyl alcohol.

The Use of Alcohol Fuels in Automobile Engines.

The physical properties of the lower aliphatic alcohols prevent their satisfactory adoption as ordinary automobile fuels in an undiluted state. A comparison of their calorific values shows that, at the same compression ratio and overall efficiency, the relative fuel consumption for a given power output are as follows:

No. 1 Grade gasoline .	100
Ethyl alcohol .	161·4
Methanol .	221·6

Apart from calorific value considerations, however, there are other difficulties to be overcome before these alcohols can be satisfactorily used as undiluted motor fuels by the ordinary motorist. The substances have very high latent heats and, in consequence, do not vaporize so readily in a carburettor as ordinary gasolines. As a result, general engine flexibility suffers to a very marked extent. Furthermore, their low vapour pressures cause greater difficulty in starting an engine from cold.

For these reasons, methanol and ethyl alcohol are only suitable as motor fuels for ordinary automobiles when diluted with normal hydrocarbon fuels, such as gasolines, and in consequence most of the work done in developing alcohol fuels has been carried out with this point in mind. As already mentioned, alcohol-gasoline blends are being adopted as standard fuels in most European countries and are meeting with some approval from the motoring fraternity. The success, or otherwise, of such alcohol fuel mixtures is naturally dependent upon their composition and the amount of alcohol they contain, but it is by no means true in every respect that the greater the alcohol concentration the less satisfactory the fuel, or vice versa.

The point of greatest value in favour of alcohol-containing motor fuels is their high anti-knock value, which enables them to be used in high-compression engines without causing knocking. This has already been dealt with and need not be discussed further, but this advantage is completely discounted if the fuels do not embody a proper combination of cost, power output, and rate of fuel consumption.

A point of outstanding importance is that concerning the relationship which exists between the alcohol content of a gasoline-alcohol blend and the fuel consumption for a given power output. If the latent heats of gasoline and alcohol were the same, this relationship would be linear for any given compression ratio, the fuel consumptions of alcohol and gasoline being inversely proportional to their calorific values. However, the large difference existing between these two substances in latent heats is almost as important as the large difference in calorific value, and it is the cause of very noteworthy, if somewhat unexpected, results.

The latent heat of vaporization of a fuel determines, to a large extent, engine volumetric efficiency and, consequently, has an effect on power output. In the case of alcohol fuels latent heat is of great importance and has a noticeable effect upon the fuel consumption for a given power output. Fig. 2 gives results obtained by Hubendick [34, 1928] in the examination of a range of gasoline-ethyl alcohol mixtures, and shows that the fuel consumption, in terms of heat units, is not appreciably greater with a 20% ethyl alcohol blend than with gasoline alone, whereas blends containing higher amounts of alcohol give fuel consumption in proportion to the alcohol content.

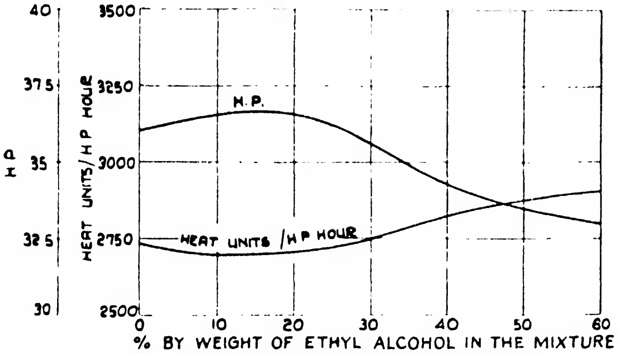


FIG. 2. Results obtained by Professor Hubendick.

As, in these tests, no changes in the engine conditions, other than an alteration in carburettor jets, were made, it follows that in blends containing up to 20% of alcohol, an increase in overall engine efficiency must be compensating for the lower calorific value. This higher overall efficiency is solely caused by the higher latent heat of the alcohol which causes the air consumption per cycle to be increased and so increases the power output. Up to alcohol concentrations of 20%, therefore, the decrease in calorific value of the fuel is compensated for by the increase in latent heat and the fuel consumption is not adversely affected, but in the case of blends containing more than 20% of alcohol, the decrease in calorific value is the determining factor and, consequently, the rate of fuel consumption increases.

Similar results have been obtained by Howes [33, 1933] in tests on methanol blends on an Armstrong-Whitworth variable compression engine. These results cover a range of compression ratios and methanol concentrations, and show that, with the somewhat over-rich fuel-air mixture used, the introduction of methanol in concentrations of up to 15% in a 30% benzole-gasoline blend, actually increases the power output and decreases the fuel consumption. More than 15% of methanol gives a higher fuel consumption.

It should be noted, however, that these results were obtained with a fuel-air mixture composition on the rich side, made to approximate as nearly as possible the mixture composition supplied by carburettors on multi-cylinder engines.

The results of tests conducted over a range of fuel-air mixture strengths are given in Fig. 3, in the form of the familiar consumption B.M.E.P. loops, and it is evident from these that the advantage in fuel consumption, obtained with fuels containing small amounts of alcohols, are only obtained at mixture strengths of richer composition than the theoretical. At weak mixture strengths the fuel consumptions are entirely dependent upon the fuel calorific value and are higher the higher the alcohol content.

Observations obtained on a benzole mixture and on a benzole mixture containing 10% of methanol at the same carburettor settings are numbered, and these clearly show the effect obtained by changing over from one fuel to the other at any mixture strength.

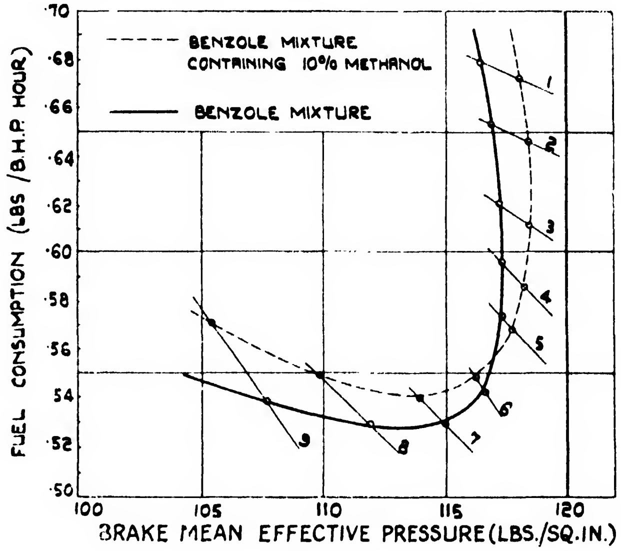


FIG. 3.

In the case of multi-cylinder engines, inequalities in fuel-air mixture distribution to the various cylinders noticeably limit the usable range of mixture strengths, and, for satisfactory operation, an over-rich mixture must be used in order to ensure that the cylinder receiving the weakest mixture is being supplied with a mixture that will fire readily and efficiently. On privately owned automobiles rather rich fuel-air mixtures are almost invariably used because they give engine flexibility over a wide range of speeds and loads, whereas, on commercial vehicles, the carburettor is adjusted to supply the weakest possible mixture, on the grounds of fuel economy and cost.

Because of these facts, it is found that alcohol fuels containing not more than about 20% of ethyl alcohol or not more than 15% of methanol give no greater fuel consumption per mile than ordinary gasolines when used in privately owned automobiles. Thus, Howes [33, 1933] has described a series of tests upon a number of different cars using (*a*) gasoline, and (*b*) gasoline plus 10% of methanol as fuels. These cars were selected haphazardly and no adjustments whatever were made to their carburettors or fuel systems. They were driven round a 17-mile circular track by their owners and fuel consumptions measured. The results of these tests show that of the ten cars used, only three gave higher fuel consumptions on the alcohol blend. Similar results have been obtained by other workers in this field.

With regard to the behaviour of alcohol fuels in ordinary automobiles, therefore, if the alcohol content is kept below 20–5% by volume (15% in the case of methanol fuels), such mixtures may be used with satisfaction without any alteration in carburettor setting and without any alteration in any way to the engine. Such blends will give approximately the same fuel consumption as ordinary gasoline, and will give about the same power output. Neither starting properties nor engine flexibility will be impaired to any marked degree. If, on the other hand, the alcohol concentration is increased above these limits, power output will be decreased and fuel consumption correspondingly increased, with the result that the blend will not give satisfaction, as instanced by the marked unpopularity of 'Carburant National', in France, which contains 50% ethyl alcohol, and the success of 'Lattbentyl', containing only 25% ethyl alcohol, in Sweden.

The Use of Alcohol Fuels in High-duty Racing Engines.

The alcohols methanol and ethanol find ready application as fuels for high-duty engines in racing events, and so on. In such applications, where fuel economy is not a major consideration and where maximum power is essential, these alcohols offer many advantages over straight hydrocarbon fuels or hydrocarbon fuels doped with anti-knock agents.

As is generally known, there is no relation between the calorific value of a fuel and the power output which may be obtained by its use, calorific value only determining the quantity of fuel required to do this work. Therefore, if fuel economy is not the prime requirement, the two factors which control power output, as far as the fuel is concerned, are (*a*) latent heat of vaporization, which determines the volumetric efficiency obtainable, and (*b*) knock rating, which determines the highest engine compression ratio which may advantageously be employed.

The lower alcohols are therefore capable of giving very high-power outputs in high-compression engines because their anti-knock properties are very good, and because their latent heats of vaporization are much higher than those of hydrocarbons. High rates of fuel consumption must, however, be employed in order to obtain this advantage, and this consideration limits the use of undiluted alcohols as fuels in racing and record-breaking events to short-distance runs. For long-distance races the high fuel consumption, which determines the amount of fuel carried by the machine consuming it, more than counterbalances the increased power output obtained, and such fuels cannot compete in general suitability with high anti-knock hydrocarbon fuels.

Little information is available concerning this special use of alcohol fuels, although Howes has described results obtained in various single-cylinder motor-cycle engines and multi-cylinder automobile engines, both supercharged and unsupercharged [33, 1933].

It is of interest to note that the air-speed record until recently held by Great Britain was obtained using a special fuel, of which methanol was a major constituent.

Of the racing fuels sold in Great Britain, a large proportion of these contain either methanol or ethyl alcohol in large concentrations.

General Properties of Alcohol-gasoline Blends.

Distillation Characteristics. Both methanol and ethyl alcohol form a whole series of constant boiling mixtures with hydrocarbons normally present in motor fuels. These constant boiling-point mixtures have boiling-points lower than those of their constituents, and as a result the distillation curves of alcohol-gasoline blends show a decided 'alcohol flat' as shown in Fig. 4, from which it is evident that the addition of 10% by volume of alcohol to a gasoline increases the proportion of material boiling at 60° C. from 6 to 10%, although ethyl alcohol itself boils at 78° C.

Measurements of Reid vapour pressure indicate an increase in vapour pressure when ethyl alcohol is added to gasoline, the maximum increase occurring when the alcohol content is 15% by volume. At this point the increase is about 1 lb. per sq. in.

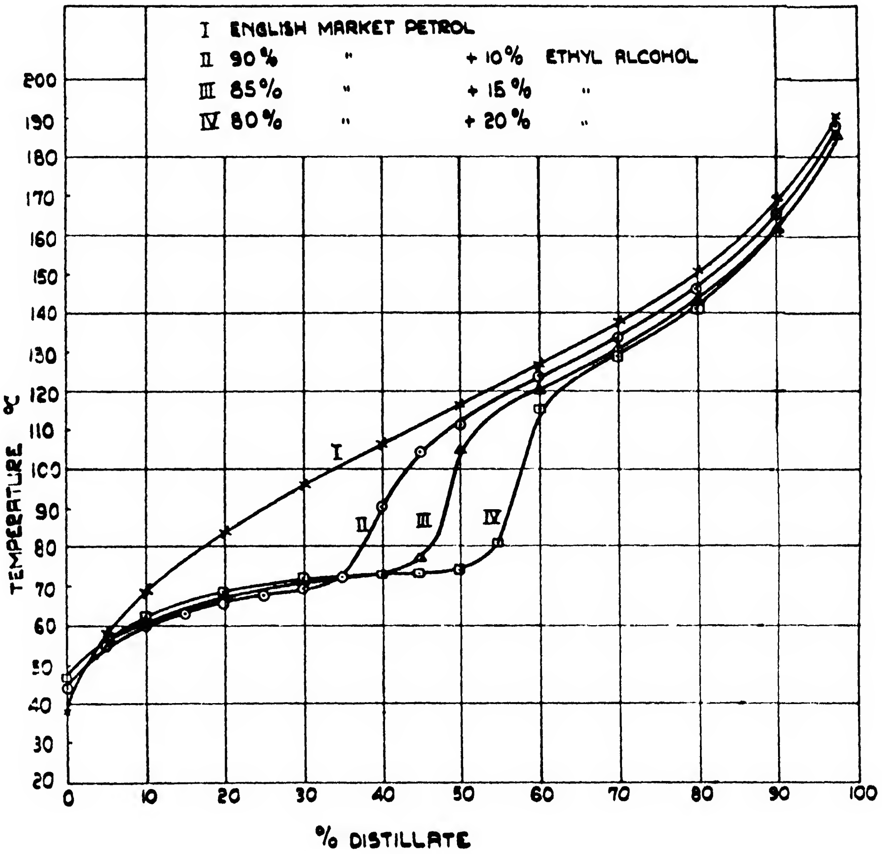


Fig. 4.

Effect on Rust, &c., deposited in Fuel Tanks. When alcohol fuels are used for the first time in an automobile that has been run on gasoline for a considerable period, trouble in the form of choked gasoline filters and carburettor jets is almost invariably caused. This is due to the fact that alcohols and alcohol-gasoline mixtures are extremely good solvents for resins deposited from gasolines and for solder fluxes, &c., left in the fuel system. They are also particularly effective in loosening rust deposits from the inside surfaces of tanks and fuel lines. Such materials quickly block up carburettor jets and choke filters inserted in the fuel lines. It is therefore necessary when changing over from a gasoline to an alcohol blend thoroughly to clean out the fuel system with the latter before putting the automobile on the road, otherwise inconvenience may be caused. Once the fuel system has been thoroughly cleaned out no further trouble results, although it recurs immediately after gasoline has been used again.

Alcohol fuels have also an extensive solvent action upon lacquers and shellacs, and if allowed to come in contact with the paint work of certain cars have a disastrous effect upon it. The case has been described of a gasoline tank varnished on the inside with a spirit varnish. When an alcohol fuel was placed in the tank, the varnish was completely dissolved and subsequently deposited in the induction pipe of the engine.

Ease of Starting and Acceleration. It has been shown that the addition of 10% of ethyl alcohol to gasoline makes it possible to start at lower temperatures than with gasoline if the atmospheric temperature is not below 0° F.; but if the atmospheric temperature is below −10° F., lower starting temperatures are possible with gasoline than with a 10% blend of alcohol and the same gasoline. When 20, 30, or 40% alcohol blends are used, the main effect is to raise the minimum temperatures for satisfactory starting above those for the 10% blends, and this effect would be very marked with the 40% blends.

In the tests carried out by the U.S. Bureau of Standards with 15 different cars (May 1933), it was found that drivers of cars reported slightly poorer acceleration with alcohol-blended fuels. Numerous experimental investigations have shown that, when the mixture ratio and the spark-setting are adjusted to optimum values, the same acceleration may be obtained with a 10% alcohol blend as with gasoline, at the expense of about 3–4% increase in fuel consumption. The increase in fuel consumption would be approximately double this amount when using a 20% alcohol blend [*2a*, 1936].

Vapour Lock with Alcohol-gasoline Blends. The tendency to vapour lock of any gasoline or gasoline-alcohol blend can be gauged from the Reid vapour-pressure value, the tendency increasing with increasing vapour pressure. It has been found that with a 10% alcohol blend the vapour pressure is increased by an average figure of 0·8 lb. per sq. in. over the vapour pressure of the original gasoline. The increase in vapour pressure in blending 20% of alcohol with gasoline is approximately 0·5 lb., and in the case of a 40% blend there is a decrease in vapour pressure of about 0·5 lb. per sq. in. on blending. However, the use of high percentages of alcohol increases fuel consumption and tends to reduce the ease of starting [*2a*, 1936].

Effect of Alcohol Fuels on Engine Temperatures. When running on alcohol fuels, engine temperatures are usually lower than when running on gasolines, and the greater the alcohol content of the blend the lower the temperature. This is due mainly to the higher latent heats of the alcohols, which give a lower induction-stroke temperature and, consequently, a slightly lower average temperature over the whole cycle, but the lower flame temperatures of alcohol fuels also play a part.

In the case of 95% ethyl alcohol, Ricardo [53, 1924] has shown that the temperature at the end of compression is about 70° C. lower than in the case of gasoline, while the maximum flame temperature attained will be, approximately, 170° C. lower. Consequently the loss of heat to the cooling water and that due to change of specific heat, &c., is substantially reduced.

Fig. 5 has been plotted from Ricardo's data and shows the heat distribution observed when running on petrol and on 95% ethyl alcohol, at a compression ratio of 5·45, and at mixture strengths giving the maximum efficiency. The horizontal scale denotes the number of B.Th.U. per hour supplied to the engine in the form of fuel, and the vertical scale the percentage accounted for in I.H.P. and cooling water. The upper curves, i.e. those referring to the heat lost in the exhaust and by radiation, are plotted by difference.

The reduction in cooling-water temperature experienced when running on alcohol blends containing up to 40% of alcohol amounts to 15° C., and may be an advantage or a disadvantage, depending upon circumstances. Thus in hot summer weather a lower radiator temperature is to be desired, especially in hilly country, but in wintry weather it may cause excessive deposition of liquid fuel upon the engine cylinder walls, and may lead to crankcase dilution, excessive lubricating-oil consumption, and poor cylinder lubrication. Because of the lower radiator temperatures obtained when running on alcohol blends, these fuels require a longer time for the engine to become thoroughly warmed up, this causing a lack in general flexibility on starting the engine from cold.

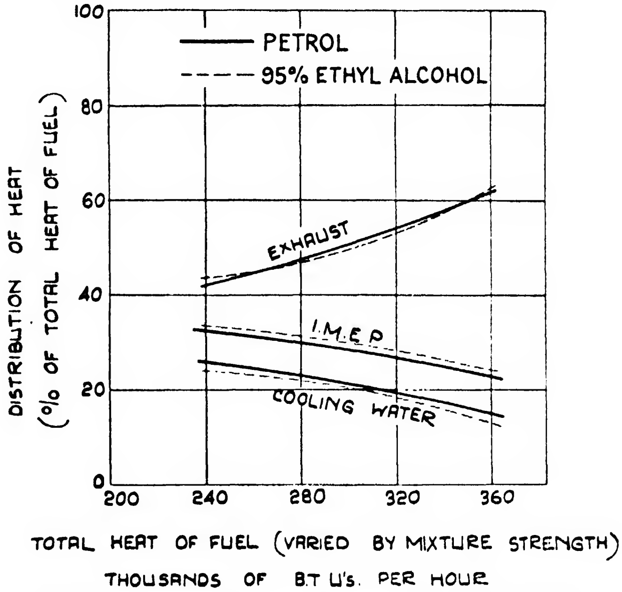


FIG. 5. Results by Ricardo. Compression ratio 5·45 to 1.

Crankcase Dilution and Cylinder Wear. Little precise information is available regarding the extent of crankcase dilution experienced with alcohol fuels, but it would appear that this phenomenon would occur to about the same extent as with petrols. With high alcohol blends, however, in which cases a large amount of liquid fuel enters the engine cylinder, crankcase dilution may be somewhat higher than normal. Harsh running, ascribed to the washing action of the fuel on the cylinder walls, has been said to be a peculiarity of alcohol fuels, but this does not find general support, although Egloff says that harshness of running is so marked when starting from cold that the engine will not deliver anything approaching its full power for some time. Examination shows that the moving parts are much drier and free from lubricant than when ordinary gasoline was used.

Carbon Formation. Little conclusive evidence on this point is available, and no reliable conclusions can be made.

Corrosive Properties of Alcohol Fuels. The aliphatic alcohols are much more corrosive to the metals commonly employed in automobile construction than normal hydrocarbon fuels and much trouble has been caused as a result. The most general trouble is corrosion of brass and aluminium carburettors, fuel lines, and fuel tanks, due to the fact that alcohols readily attack aluminium (and more particularly magnesium) to form alcoholates and hydrogen. In the case of brass, the corrosion appears to be accelerated by electrolytic action and the presence of metallic couples. Methanol blends are much more corrosive to the above metals than ethyl alcohol blends. In the case of carburetted alcohol-air mixtures, these are normally no more corrosive than the corresponding hydrocarbon-air mixtures. Exhaust gases from alcohol fuels are definitely corrosive at temperatures below the dew-point because of the presence of organic acids.

Gaseous Fuels

The following gaseous fuels have been considered in some detail as possible fuels for spark-ignition internal-combustion engines:

1. Town's gas.
2. Hydrogen.
3. Paraffin and olefine gases derived from petroleum.
4. Producer gases.

These may conveniently be considered in this order.

Town's Gas.

The use of town's gas as a fuel for high-speed internal-combustion engines dates back to pre-War days, when, as at present, large quantities of town's gas were used for the 'running in' of high-speed engines primarily designed for running on petrol.

In those days the compression pressures used in engines of this type were comparatively low, with the result that when running on town's gas the maximum power developed did not reach that obtained with gasoline.

During the period of the War many types of vehicles were run on gas, owing to the shortage of gasoline, the gas begin stored in the majority of cases in large flexible bags, usually housed on the roof of the vehicle, and where the compression ratios of the engines were reasonably high the thermal efficiencies realized were of a high order.

The main difficulty which presented itself, however, was the somewhat limited capacity of fuel storage, which resulted in the radius of action of the vehicle being somewhat restricted.

At that time the possibility of storing gas in the compressed form in steel cylinders was given serious consideration, but it was found that this scheme was impracticable owing to the weight of the containers being too great in comparison with the amount of gas stored.

During the last 10 years a considerable amount of research work has been carried out in England and also in Europe in connexion with the manufacture and use of high-tensile alloy-steel cylinders, made from nickel-, nickel-chrome-, and nickel-chrome-molybdenum steels and of sufficiently low weight to enable a vehicle to carry a reasonable supply of high-pressure gas. In England the City of Birmingham Gas Department have been very active in encouraging the use of compressed town's gas in automobiles, while in France the Societé du Gaz in Paris have also carried out much original work on the same lines. In Germany the Stuttgart Gas Works have been supplying consumers with compressed town's gas for some time.

The investigations carried out by the City of Birmingham Gas Department have been very complete, and the results obtained may be described in some detail as being representative of general experience. In a paper published by C. M. Walter [62] in 1932 the following conclusions were arrived at as a result of work done to that date.

1. The thermal efficiency of high-speed internal-combustion engines when supercharged is greater when using town's gas than when gasoline is used, and is further increased by carburetting the gas with benzole.
2. The thermal efficiency with gasoline as a fuel is decreased by the application of supercharging.
3. The maximum power developed with gas alone is lower than that obtained with gasoline.
4. The carbon monoxide content of the exhaust gases is considerably less with town's gas as a fuel than in the case of gasoline.
5. Gas is more responsive to supercharging than gasoline, the power output being increased to a greater extent. This is corroborated by the fact that with supercharging the thermal efficiency is only decreased by 0·25% on town's gas compared with 6·45% on gasoline.
6. The thermal efficiency obtained with town's gas is further increased by increasing the compression ratio. (Note: this applies to gasoline also.)
7. The performance of the engine is very much improved by saturating the gas with gasoline or benzole, the amount of gasoline required being about 0·75 gal. per 1,000 cu. ft. of gas.

From these results it may be assumed that with a standard type of engine having a compression ratio of 5 to 1, 1 gal. of petrol would give about the same performance under average conditions of running as 265 cu. ft. of gas of 475 B.Th.U. per cu. ft. calorific value—this figure being reduced as the compression ratio is increased. It would also appear that in the case of gas carburetted with benzole, this figure would be reduced to about 200 cu. ft., the carburetted gas having a calorific value of 575 B.Th.U. per cu. ft.

In 1933 Walter [63] described further work, a short summary of which is as follows: Experimental work was carried out on the compression of town's gas and the use of light-weight storage cylinders suitable for mounting on vehicles for storing the gas at working pressures up to 3,000 lb. per sq. in.

The dimensions of these cylinders approximate to 8 in. outside diameter and 73 in. long, with a wall thickness of 0·22 in. The internal volume is 1·76 cu. ft., and thus at a working pressure of 200 atm. the volume of free gas contained is about 352 cu. ft., and the approximate weight of each bottle empty is 119 lb. The number of bottles carried depends on the size and type of vehicle.

Alloy-steel bottles of this type are being manufactured by Vickers-Armstrong, Limited, Newcastle-on-Tyne, and the Chesterfield Tube Company. In the case of a test specimen from a bottle made by the former firm the following results were obtained:

Ultimate strength	67·9 tons per sq. in.
Yield	59·5 „ „
Impact	53·0 ft. lb.
Elongation	22·8%
Reduction of area	59%

Bending test: Bent through an angle of 180° without cracking. Limit of proportionality, i.e. maximum stress at which strain is proportional to load, 47 tons per sq. in.

In the case of vehicle bottles with a working pressure of 3,000 lb. per sq. in., the wall thickness is such that the maximum working stress is 25 tons per sq. in., whilst in the case of the stationary storage cylinders where a working pressure of 5,000 lb. per sq. in. is employed, it is proposed that a working stress of not more than 16·7 tons per sq. in. should be employed, this giving a factor of safety of three in the case of cylinders heat treated to give an ultimate strength of 50 tons per sq. in.

Vehicle Equipment. The complete equipment necessary to operate a vehicle on town's gas includes:

A battery of storage cylinders of the type already described, suitably attached to the chassis frame and interconnected by means of solid-drawn steel pipes fitted with suitable valves of forged steel.

The number of storage cylinders employed will, of course, depend on the type and weight of vehicle and the mileage required from a single charge.

Further, a suitable reducing valve to reduce the pressure from the working pressure in the storage cylinders to any desired pressure at the engine inlet is required, in addition to an air-gas mixer which takes the place of the ordinary carburettor.

The usual form of reducing valve employed consists of a two-stage diaphragm type, so designed as to reduce the pressure from, say, 3,000 lb. per sq. in. to 5 lb. per sq. in. in the first stage, and from 5 lb. per sq. in. to any pressure that may be required at the air-gas mixer in the second stage.

The valve areas are such that at all loads the requisite flow of gas into the induction system is maintained.

With the system at present employed the pressure of the gas is reduced to sub-atmospheric in the second stage of the reducing valve, in order to ensure that when the engine is stationary the supply of fuel is automatically cut off, as the second-stage valve will only operate when under the influence of the depression caused in the induction system by the engine suction. It might, however, be desirable with certain designs of engines to arrange for the gas to be supplied at a slight positive pressure in order to maintain a high volumetric efficiency over a wide range of loads. In the latter case, the gas and air required would be admitted to the cylinders through independent valves, and not as an admixture.

With regard to air-gas mixers, the results of experimental work carried out with engines on bench tests and also on vehicles running under service conditions indicate that when the gas and air are admitted to the induction system by means of a choke, the most satisfactory way of obtaining the best admixture of air and gas is to reduce the gas pressure to atmospheric pressure or slightly below and to depend on the suction of the engine to cause both air and gas to be induced into a choke tube of suitable dimensions, where intimate mixing takes place. In the case of certain designs of engines, it has also been found to be advantageous to introduce velocity tubes in the induction manifold further to assist admixture of gas and air by bringing them more into intimate contact.

The type of mixer at present employed consists of a Venturi choke tube through which the air is drawn, the gas entering through ports, in the form of slots, arranged at right angles to the air stream, these ports being suitably placed circumferentially around the contracted section of the choke tube itself.

The advantage of being able to ensure a constant air-gas ratio over a wide range of speeds with this simple type of mixer will be apparent, as the volume of gas and air induced into the induction system will follow closely the square root law, the proportion of air to gas thus remaining constant over a wide range of throttle opening.

An economic study of the possible use of compressed town's gas as a substitute for petrol has recently been presented by Cook [8, 1936], who points out, quite rightly, that the fundamental objection to the use of compressed gaseous fuels is the difficulty of carrying sufficient gas for economic mileage range, as the radius of action of a gas-propelled vehicle is restricted by the size and weight of storage cylinders to some 60–70 miles on a single charge. Cook concludes that gaseous fuels cannot compete economically with Diesel oil at its present price, and would only show to advantage if the price of Diesel fuel rose considerably. Moreover, it is concluded that, taking all relevant charges into account, compressed gas can only compete with petrol fuel in the case of vehicles of less than 2 tons capacity. The truth in such conclusions is borne out by the fact that at the present time there are only about 24 gas-driven vehicles on the roads of the United Kingdom—although gas-filling stations are available at both Birmingham and Chesterfield. The reason for the lack of development is the advance of the Diesel engine—especially for buses and heavy, long-distance lorries.

Hydrogen as a Fuel for Internal-combustion Engines.

A very early attempt at producing an internal-combustion engine proposed the use of hydrogen as a fuel. In 1820 the Rev. A. Cecil read a paper before the Cambridge Philosophical Society on 'The Application of Hydrogen Gas to produce a Moving Power in Machinery'. This engine followed current practice and depended on atmospheric pressure and the partial vacuum produced by the explosion of hydrogen in air. The engine is said to have run satisfactorily. Very little more attention was given to the use of hydrogen as a fuel until quite modern times. A new impetus was given by the possibility of using hydrogen as an additional fuel in the gasoline or Diesel engine used in lighter-than-air aircraft, rather than releasing the hydrogen to waste, as progressive fuel consumption lightens the airship.

In Aeronautical Research Committee Reports and Memoranda no. 1029 experiments are described on the use of hydrogen in this way. Hydrogen was not considered by the experimenters as likely to increase the thermal efficiency of the gasoline engine. On the other hand, Ricardo [53, 1924] has called attention to the very wide range of weak mixtures of air and hydrogen that can be used, enabling power output to be controlled by the quality of the charge. With a rich mixture, even at a compression ratio as low as 3·8 to 1, violent pre-ignition was observed accompanied by firing back into the carburettor. Very good results were obtained at a compression ratio of 7 to 1, provided the I.M.E.P. was maintained below 74 lb. per sq. in.; at this point detonation occurred.

Most of the experimental work reported on the use of hydrogen as a fuel has been conducted by the Erren Motoren G.m.b.H., an account of which has been given by Erren and Campbell [22].

Paraffinic and Olefinic Gases derived from Petroleum, &c.

Experiments were carried out in Germany some years ago to obtain a gas fuel suitable for use in airship engines. As the production of a gas consisting of one chemical entity presented difficulties, 'Blaugas' was considered the most suitable and was ultimately used satisfactorily. The first stage of its manufacture consists in the production of 'Pintsch Gas' by cracking a mineral oil such as 'mineral seal oil', Scotch shale oil, or Russian Solar oil at 600–

700° C. The resultant gas, freed from carbon dioxide and sulphur compounds by lime treatment, is compressed to about 10 atm., when a small proportion of liquid hydrocarbons separates. The gas is then compressed to 100 atm. and cooled, and yields a liquid consisting of ethane, propane, butane, propylene, and butylenes with ethylene and methane in solution. This liquid is 'Blaugas' and contains 39% paraffins; it can be used at compression ratios up to 9 to 1. In America suitable fuel of a similar composition has been prepared from natural gas by similar methods. Under the name 'Pyrofax' liquefied propane containing about 2% butane has been marketed in U.S.A. The Graf Zeppelin has used this fuel in some of its flights, sometimes mixed with hydrogen and sometimes with natural gas.

Detailed experiments on the use of oil gas as a fuel have been described by Helmore [32]. Using a gas containing 49% methane, 36% ethylene, and 6% hydrogen, very promising results were obtained. In a Ricardo E. 35 engine it was found impossible to cause back-firing into the fuel intake with this gas either by varying mixture strength or engine speed, the engine being capable of being brought to a standstill by this means at either end of the mixture range. No signs of detonation or pre-ignition were observed at 7:1 compression ratio. Engine tests carried out with this fuel on a Rolls-Royce 350-h.p. aero-engine confirmed the single-cylinder results, the absence of detonation and tendency to misfire being maintained. Very smooth running and improved distribution were obtained, whilst easy starting and flexible control over the whole mixture range was found to result. Satisfactory results on oil-gas kerosine mixtures were also obtained.

Vogt [61, 1935] has described engine tests on butane fuel. Using a single-cylinder variable compression engine, he found that it was possible to increase the compression ratio appreciably over that allowable when operating with gasoline, but the fuel consumptions were higher with butane than with gasoline under comparable conditions. This agrees with general road experience. The maximum power output was greater with butane.

The liquefied gas industry in America is undergoing great expansion, the products being used mainly in domestic heating appliances, oven-heating, and metal-cutting. Liquefied gases—both propane and butane—are sold in large quantities at 5–10 cents per gallon. Distribution is effected in tank cars and truck units.

In the United Kingdom liquefied butane has recently appeared on the market, while in France butane has been sold for some years. In Germany liquid propane has been marketed by the I.G. for some time. In steel cylinders of similar capacity, propane gives 10 times the quantity of heat available from town's gas compressed to 150 atm.

With regard to the utilization of such fuels for internal-combustion engines, the octane numbers are of considerable importance. The following values have been reported [27, 1932]:

Blending Octane Numbers

	212° F. jacket temp.	*300° F. jacket temp.*
Ethylene	85·5	82·5
Propylene	102·0	94·5
1-Butene	111·5	95·0

n-Butane has an octane number of 91, and iso-butane an octane number of 99 [48, 1936].

Producer Gases as Engine Fuels.

With regard to this development, numerous difficulties are encountered, due to the slowness of operation of the gas generator and to impurities in the resulting gas. The weight of the generator and the weight of the solid fuel carried is also a disadvantage.

The equipment consists essentially of a small gas producer and a gas scrubber. The former comprises a fuel hopper and a small, refractory, lined, insulated, combustion chamber, which is fitted with a grate which must be designed to avoid difficulty from clinkering. Webster [64, 1932] has described such an arrangement for burning low-temperature coke, in which the producer can be operated on up-, down-, or combined draught. Water flows into a vaporizer above the refractory or into the annular space around the base, according as the draught is up or down. The gas cleaner and scrubber consist of an oblong box fitted with shutters through which the gas passes, after which it is filtered through wood wool before it passes to the engine. The generator is operated by the engine suction. A fire of wood sticks is started in the combustion chamber, the hand blower is used for a few minutes, and the hopper is fitted with coke. The engine is started on spirit, and after running a few moments is switched over on to gas.

The coke requirements of such small producers are stringent. Suitable cokes are those that are high in volatile content, low in moisture, and of low ash content. Gas coke is not suitable. According to Webster, with low-temperature coke at 30*s.* per ton, the fuel cost per B.H.P.H. is 0·176 pence, whereas, with motor fuel at 1*s.* per gallon, the fuel cost is 1·024 pence per B.H.P.H.

Details concerning the sizes of the producers used on automobiles in this way have been given by Charles-Roux [6, 1931].

Raw wood and wood charcoal have been used as gas-producing materials. The former, however, gives rise to troublesome tarry substances carried away in the gas. Charcoal is the cleanest fuel to employ.

To obtain satisfactory results with such gaseous fuels, the engines must be modified to run at a higher compression ratio and a greater degree of turbulence in the cylinder head. The power output from a normal gasoline engine is reduced when running on gaseous fuels. Figures have been quoted regarding a test in a four-cylinder Chevrolet vehicle, 94-mm. bore and 102-mm. stroke, which, when operated on gas from birch wood containing 20–30% moisture, gave 40% less power than with gasoline at a compression ratio of 4·64. When the latter was raised to 6·1, the decrease in power was still about 20%. One kilogram of wood was found to be equivalent to 210 g. of motor spirit [42, 1930].

Apart from a slight saving in fuel cost, such producer-plant equipment has nothing to commend it. It is heavy, cumbersome, and unsightly, and it materially reduces the overall reliability of the motor vehicle. On the other hand, the use of portable producer-gas plants of this type has been advocated by Russell [55, 1933].

REFERENCES

1. AUDIBERT, E. *Chem. et Ind.* **13,** 186 (1925).
2. *Brenn. Chem.* **7,** 97 (1926); *Ber.* **59,** 830 and 832 (1926).
2*a*. BRIDGEMAN, O. C. *Ind. Eng. Chem.* **28,** 1102 (1936).
3. BUC, H. E., and ALDRIN, E. E. *Nat. Petr. News,* **28** (25), 25 (1936).
4. BURY. *Cleveland Institute Eng. Gas J.* **148,** 718 (1919).
5. BYRNE, P. J., GOHR, E. J., and HASLAM, R. T. *Ind. Eng. Chem.* **24,** 1129 (1932).
6. CHARLES-RAUX. *Chim. et Ind.,* **25,** 245, Special No. (March 1931).
7. *Colliery Guardian,* **135,** 249 (1927).
8. COOK, R. *Petr. Times,* **35** (894), 273 (1936).
9. DAMIENS, A. *Bull. Soc. Chim.* **33,** 71 (1923).
10. DAMIENS, A., and PIETTE, O. J. G. B.P. 180,988 and 152,495.
11. DAVIS, H. S., and Petroleum Chemical Corporation. B.P. 248,375 and 249,834.
12. DAVIS, H. S., and SCHULER, R. *J.A.C.S.* **52,** 721 (1930).
13. DUNSTAN, A. E., and HOWES, D. A. *J.I.P.T.* **22,** 347–413 (1936).
14. ELLIS, C. *Chem. and Met. Eng.* **23,** 1230 (1920); B.P. 146,957 (1920).
15. ELVINS, O. C., and NASH, A. W. *Fuel,* **5,** 263 (1926); *Nature,* **118,** 154 (1926).
16. ENSOR, G. L. *J.I.A.E.* **3,** no. 9, 13–16 (1935); *J.I.P.T.* **21,** 315A (1935).
17. B.P. 323,748.
18. B.P. 381,723.
19. B.P. 336,633 and 336,603.
20. B.P. 368,051.
21. ERDELY, A., and NASH, A. W. *J.S.C.I.* 47, 219–23T (1928).
22. ERREN, R. A., and CAMPBELL, W. H. *J. Inst. Fuel,* **6,** 277 (1932–33).
23. FISCHER, F. *Brenn. Chem.* **16,** 1–11 (1935).
24. FISCHER, F., BAHR, T., and MEUSEL, A. *Ber.* **69** B, 183–6 (1936).
25. FISCHER, F., and MEYER, K. *Brenn. Chem.* **15,** 84–93 and 107–10 (1934).
26. FISCHER, F. and TROPSCH, H. *Brenn. Chem.* **4,** 276 (1923); **5,** 201 (1924). FISCHER and LESSING. *The Conversion of Coal into Oils* (1925).
27. GARNER, F. H., WILKINSON, R., and NASH, A. W. *J.S.C.I.* **51,** 265–71T (1932).
28. GERR, V., and POPOV. *Neft. Choz.* **10,** 88 (1926).
29. GERR, V., PIPIK, O., and MEZHEBOVSKAYA, E. *Neft. Choz.* (2), 15–21 (1932).
30. GLAUD and others. *Ber. Ges. Kohlentechnik,* **4,** 210 (1923).
31. HALL, F. C., WIGGINS, W. R., and NASH, A. W. *J. Inst. Fuel* (Dec. 1935).
32. HELMORE, W. Aeronautical Research Committee. R. & M. no. 1265.
33. HOWES, D. A. *J.I.P.T.* **19,** 301 (1933).
34. HUBENDICK, E. *World Power Conference,* **3,** 724 (1928).
35. *Industrial Chemist* (Apr. 1928).
36. JOSHUA, W. P., and STANLEY, H. M. The Distillers Company Limited. B.P. 370,136.
37. *J.S.A.E.* **39** (1), 52–6 (1936).
38. KLEIN, F. D. *Oil and Gas J.* 40 (7 Feb. 1935).
39. KOCH, H., and IBING, G. *Brenn. Chem.* **16,** 185–90 (1935).
40. KOCK, H., PICHLER, H., and KOLBEL, H. *Brenn. Chem.* **16,** 382–7 (1935).
41. KUHRING, M. S. *Canad. J. Res.* **11,** 489 (1934).
42. KYRKLUND, H. *Z. angew. Chem.* 698 (1930).
43. MAREK, L. F., and HAHN, D. A. *Catalytic Oxidation of Organic Compounds in the Vapour Phase,* 226 (The Chemical Catalogue Co. 1932).
44. MONIER-WILLIAMS. *Power Alcohol,* 92–8 (1922).
45. MYDDLETON and WALKER.
46. NASH, A. W., and HOWES, D. A. *Principles of Motor Fuel Preparation and Application,* **1,** 2nd ed. (Chapman & Hall Ltd.).
47. NATHAN, Sir F. *World Power Conference* (1928).
48. NEPTUNE, F. B., TRIMBLE, H. M., and ALDEN, R. C. *Oil and Gas J.* **34** (49), 26 (1936).
49. OSTERREITH, J. W., and DECHAMPS, G. *J. Inst. Fuel,* **6,** 215 (1933).
50. PATART, G. *Chim. et Ind.* **13,** 179 (1925).
51. PICHLER, H. *Brenn. Chem.* **16,** 404–6 (1935).
52. PIER, M. *Colliery Guardian,* 433 (8 March 1935).
53. RICARDO, H. R. *Empire Motor Fuels Committee Report,* 144 (1924).
54. ROSS, J. D., and ORMANDY, W. R. *J.S.C.I.* **95,** 273T (1926).
55. RUSSELL, J. *Proc. World Petr. Cong., London,* **2,** 769 (1933).
56. SABATIER, P., and SENDERENS, J. P. *Ann. Chim. Phys.* (8), **4,** 418 (1905).
57. SPIERS, H. M., and SMITH, E. W. *Report on the Use of Coal Tar Oils in Internal Combustion Engines.* Copyright Publication no. 95 of the Institution of Gas Engineers.
58. STANLEY, H. M. Youell and Dymock, *J.S.C.I.*
59. TAYLOR, E., and WILLIAMS, G. L. *J.S.A.E.* 345 (1931); **30** (1), 24 (1932).
60. TIDMAN. *J.S.C.I.* **40,** 86 (1921).
61. VOGT, C. J. *Refiner,* **14,** 542 (1935).
62. WALTER, C. M. Copyright publication no. 48, Institution of Gas Engineers.
63. —— *Proc. World Petr. Congr.* (London, 1933).
64. WEBSTER. *J.S.C.I.* 72 (1932).
65. WILLIAMS. *Chem. Trade J.* 335 (10 Nov. 1933).
66. WOOD, H. *J.S.A.E.* **39,** 267 (1936).

INDUSTRIAL PETROLEUM SOLVENTS AND WHITE SPIRITS

By F. N. HARRAP, M.Sc., M.Inst. P.T.

Chief Chemist, Shell Mex and B.P. Ltd.

Introduction

THE motor spirits marketed generally to-day have an average boiling range of, say, 35 to 200° C. and, speaking broadly, they do not differ to any considerable extent as regards volatility. Certainly the premium grades are more volatile than the cheaper grades, but the variations in volatility or boiling range between the different spirits used for transport purposes are much less than the variations between the different types of solvent spirits. Such petroleum solvents may vary in volatility from the 60/80° C. spirit used for perfume extraction to the white spirit used in oil paints, with an approximate boiling range of 150/200° C.

It would naturally be to the advantage of the supplier if the number of different grades were minimized, but this is a difficult problem since the requirements of different industries are so varied that many different types of spirit must be available. Moreover, even for the same purpose, the larger buyers usually have their own specifications, with which their purchases must obviously conform. For these reasons the number of available grades of petroleum solvents must always be considerably higher than the number of transport grades, and because of this fact, combined with the relatively small manufacturing yields, and the necessity for segregated storages to avoid contamination, the solvent spirits must be more expensive than the transport spirit grades.

Manufacture.

As the quantities involved are, from a refinery standpoint, comparatively small, the different 'cuts' are usually produced by periodic or batch distillation, in stills fitted with fractionating columns. Where larger quantities are required, e.g. with white spirits, distillation may be carried out in a continuous type still. Since distillation of the basic spirit cannot be stopped whilst a laboratory analysis is being carried out, it follows that the only control test during the distillation must be a check of the specific gravity of the distillate coming from the still, but experience of previous distillations will enable an operator to know exactly when to change over from one grade to another. Two receivers are necessary for each grade so that delivery can be effected from the receiver, containing tested material, whilst the stock in the second receiver is being built up from the stills. Separate lines and pumps are usually necessary for each grade, so as to avoid any contamination between grades.

Types of Solvent Spirits Available.

It is impossible to give anything like a complete list of the many different spirits available, since these differ considerably in distillation range, and also in composition according to the nature and origin of the basic spirit from which they are distilled, apart from which many of them are given a more or less intensive treatment with sulphuric acid and/or oleum to reduce the aromatic content or to improve the odour. The following table will give an indication of the diversity of types of solvent which have been produced to meet industrial requirements.

Typical Petroleum Solvent Spirits

Type	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*
Sp. gr. at 60° F.	0·685	0·768	0·792	0·800	0·864	0·710	0·704	0·760
Distillation:								
Initial boiling-point (° C.)	35	75	100	115	185	70	45	110
10% distilling to (° C.)	45	..	..	..	193	..	62	117
50% distilling to (° C.)	57	80	108	129	196	76	80	123
90% distilling to (° C.)	69	..	..	..	201	..	95	137
Final boiling-point (° C.)	86	95	120	160	210	90	115	160
Flash-point (closed) (° F.)	below 73	below 73	below 73	45 app.	154	below 73	below 73	below 73
Aromatics (% by wt.)	..	25	43	40	60	2	7	12
Kauri butanol number	..	49	56	53	56	32	32	37
Dilution ratio (butyl acetate)	..	1·55	1·65	1·6	1·65	1·22	1·22	1·25
Dilution ratio (ethyl acetate)	..	..	1·55	1·55	..	1·15	..	..

Solvents 2, 3, and 4 are produced from a basic spirit rich in aromatic hydrocarbons, whilst solvents 6, 7, and 8 are made from a basic spirit of relatively low aromatic content. Solvent 6 is given a fairly intensive oleum treatment.

The Kauri butanol numbers quoted have been determined by the usual method, whilst the dilution ratios have been obtained using the method described by Durrans in his book *Solvents*.

Applications of Petroleum Solvents

Perfume Extraction.

The flower petals are extracted with cold solvent in a closed apparatus, the solvent then being separated by distillation, leaving a perfumed wax. The extracted perfumes are chemically very unstable, and a low-boiling solvent of type 6 is employed, free from sulphur and unsaturated bodies and of low aromatic content.

Seed Extraction.

The oil from oil-bearing seeds, e.g. cottonseed, rape, linseed, and castor, is removed from the seeds either by pressure in a hydraulic press or by extraction with a suitable solvent. Usually the processes are combined, the residue from the press being extracted with a close range petroleum solvent. Linseed, for example, contains about 36% of oil, and hot expression removes about 26%, leaving 10% to be extracted by solvent. It is essential to use a spirit of good odour, free from unsaturated bodies, but opinions differ as to whether an aromatic type solvent is necessary. The usual solvent is type 6, although many buyers employ a less volatile solvent.

Allied to the extraction of oils from seeds is the extraction of cocoa butter from the cakes or pulp obtained by pressing cocoa beans. The type of solvent used is similar to that used in oilseed extraction, and here again a solvent free from unsaturated hydrocarbons is essential.

Bone Degreasing.

Bones and other animal refuse are the raw material used for the manufacture of animal glue, bone manures, and bone fertilizers. The bones are crushed and are then extracted in a suitable steam-heated extractor with a solvent spirit. The solvent removes the oil and grease, the extract being run off and distilled with steam to yield fatty material, which is then distilled to give a white fatty acid used in candle manufacture.

In the extraction of bones it is essential to use a solvent with an end point not exceeding, say, 105° C., since the solvents of higher end point tend to dehydrate the glue substance unduly, giving a product of inferior adhesive quality. On the other hand, the boiling-point of the solvent must be sufficiently high to ensure that the bones are gradually dried during the extraction, so that the solvent may have a chance to extract the fats completely.

Other refuse such as fish offal or the waste food from restaurants is treated in a similar manner to produce fish meals, poultry foods, &c.

Dehydration of Alcohol.

When a mixture of alcohol and water is distilled a constant boiling mixture of approximately 95½% alcohol content is produced, but if a third liquid, e.g. benzol, is introduced the result is a ternary mixture of the approximate composition 7½% of water, 74% benzol, 18½% alcohol, this mixture boiling at 64·9° C., a temperature below the boiling-point of any of the three components. By this means it is possible to distil off practically all the water, leaving behind an alcohol of 99·9% strength.

In practice it is usual to employ, as the third liquid, not benzol alone but a mixture of 2 volumes benzol, 1 volume petroleum solvent, the latter of distillation range 90/100° C. or 90/105° C.

The ternary mixture from the rectifying still is condensed and separated, the mixture of benzol and petroleum solvent being returned to the rectifying still, and the aqueous alcohol being concentrated by distillation to about 94% strength before going back through the cycle. By using a mixture of benzol and petroleum solvent, instead of straight benzol, the separation of the aqueous alcohol layer during condensation of the ternary mixture is facilitated, and the purity of the anhydrous alcohol from the rectifying still is slightly increased.

Cellulose Lacquer Diluents.

Nitrocellulose lacquers consist essentially of nitrocellulose dissolved in comparatively expensive organic solvents, together with resins, plasticisers, and, in the case of coloured lacquers, pigments. The solvents can be divided into three general classes, the alcohols, esters, and ketones, and since no one solvent combines all the properties which are desirable, a mixture of solvents must be employed.

In order to cut down production costs it is customary to include in the lacquer formula a proportion of diluent, either of petroleum or coal-tar origin. It must be appreciated that these diluents are actually diluents and not true solvents and the percentage employed is limited by this fact, since excess of diluent throws the nitrocellulose out of solution. For this reason the diluent must be so selected, both as regards quantity and quality, that it evaporates at the same rate as, or rather more rapidly than, the true solvents in the lacquer. If the diluent is too volatile, pinholes or blisters may be produced when the lacquer film dries, but if it is of too low volatility and evaporates more slowly than the true solvents there will be an over-concentration of diluent in the film as it dries and the nitrocellulose will be thrown out of solution, giving rise to what is known as 'blushing'.

It is usual to employ petroleum diluents of comparatively narrow distillation range, with a volatility comparable with that of coal-tar toluol, and with an aromatic content as high as possible. Generally speaking, the higher the percentage of aromatics the greater is the proportion which can be included in a lacquer without precipitation of the nitrocellulose, i.e. the greater is the so-called 'dilution ratio' of the product. The main types of diluent used are distillates of high aromatic content, e.g. types 2, 3, and 4 previously mentioned. These solvents correspond approximately in evaporation rate with coal-tar benzol, toluol, and solvent naptha respectively.

It is of interest to note that special restrictions were introduced by the Cellulose Solutions Regulations, 1934, as regards the use of benzol (because of its toxic properties), and if the benzol content of a cellulose solution is more than 15% by weight the receptacles must be legibly marked as containing benzol.

Printing Inks.

The problems of the photogravure ink industry are, in so far as the choice of a suitable solvent is concerned, very similar to those of the maker of cellulose lacquers. The essential properties are a satisfactory rate of evaporation and as high an aromatic content as possible. Solvents of the types 2, 3, and 4 are used, type 2 being employed where a very volatile diluent, for high-speed printing, is necessary. In the In-tag process, for example, where 40,000 copies an hour may be produced, the paper travels at the rate of 1,200 ft. per second and the ink must dry off completely in a fraction of a second.

The Rubber Industry.

Various types of petroleum solvent are utilized in the different branches of the rubber industry. Large quantities are consumed by the tyre manufacturers and by the rubber-proofing industry and smaller, but still appreciable, amounts by makers of golf balls, tennis balls, rubber gloves, &c.

Petroleum solvents for the rubber industry should be free from very volatile fractions which lead to increased evaporation losses and enhanced fire risks, and also free from very heavy or high-boiling fractions which cannot easily be removed from the finished goods. In consequence, the spirit employed for rubber proofing, in the manufacture of such goods as waterproof garments or ground-sheets, is a product as shown under type 4. Where the proofing machines work very rapidly, or where the length of travel of the proofed cloth before it is rolled is unduly short, a more volatile solvent (type 7) is used.

Petroleum solvents have replaced almost entirely the coal-tar solvents which were formerly used in rubber proofing. The main reasons for this are (*a*) a more carefully controlled distillation range and evaporation rate, (*b*) absence of complex sulphur bodies and unsaturated hydrocarbons which might affect the ageing properties of the rubber, and (*c*) their lower toxicity, a factor of importance in badly ventilated or congested workshops.

In the cold-cure process allied to rubber proofing some manufacturers have had a certain measure of success with a solution of sulphur chloride in a volatile solvent of types 1 or 2 instead of in the more conventional carbon disulphide.

The solvents used by the tyre industry differ very considerably, many of the buyers having their own specifications, particularly with concerns subsidiary to, or allied with, tyre manufacturers abroad. Some makers use a spirit of the Aviation type with distillation range 40/150° C., others a narrow cut as type 3, still others a heavier cut as types 4 and 8.

The Leather Trade.

A solvent of narrow distillation range (type 3, for example) is used in the leather trade for what is known as 'benzine degreasing', and large quantities of solvent are used in the boot and shoe industry in the form of so-called rubber cements.

In the manufacture of boots and shoes a volatile solvent is necessary for making up the rubber solutions used as cements, type 7 being a typical solvent. Solvents of low aromatic content are usually favoured, firstly because of their less strong odour and secondly because such cements do not penetrate the leather, with a risk of consequent staining, to the same degree as cements made up with highly aromatic solvents.

Dry Cleaning.

In dry cleaning, the soiled articles are treated in mechanical washers similar to those used in laundries, petroleum spirit being used instead of water. From the washer the goods are transferred to centrifugal extractors, where the spirit is separated and subsequently recovered and put back into circulation. The recovery is effected by distillation, although some plants combine redistillation with a chemical decolorizing process.

Some of the smaller dry cleaners use ordinary motor spirits, but the larger dry cleaners use white spirit, with initial boiling-point about 150° C. and final boiling-point about 195° C. The white spirits, with flash-points over 73° F., come outside the restrictions of the Petroleum Consolidation Act of 1928, so that a user of white spirit does not have to conform with the requirements of that Act as regards storage licences, &c.

Typical White Spirits.

Type	*A*	*B*	C
Specific gravity at 60° F.	0·765	0·784	0·815
Initial boiling-point (° C.)	151	153	154
10% distilling to (° C.)	158	158	159
50% ,, ,, (° C.)	166	167	166
90% ,, ,, (° C.)	180	182	176
Final boiling-point (° C.)	193	196	194
Flash-point (° F.)	98	98	98
Sulphur (%)	0·01	0·01	0·01
Kauri butanol number	32	34	46
Aromatics (% by weight)	16	18	45

Type A is produced from a highly paraffinic crude, type C from a highly aromatic crude, whilst type B is made from a crude of intermediate character.

Paints and Varnishes.

The main application of white spirit is its use as a thinner in paints and varnishes. Originally it was introduced as a substitute for American turpentine and was marketed as 'turpentine substitute', but white spirit has proved itself the equal of genuine turpentine and now sells on its merits.

White spirits, apart from having the correct boiling range and evaporation rate, must have a good odour and be free from deleterious sulphur compounds which might affect the colour of the pigment (particularly lead pigments) in the paint. They must also be free from any grease or non-volatile residue.

Where synthetic resins are being used as a constituent of a paint it is essential to use a white spirit of high aromatic content, since otherwise precipitation of the resins might occur. A product such as that shown earlier as type 5 has been used successfully in such cases.

Other Applications of White Spirit.

Amongst the many applications for white spirit, apart from its use in oil paints, are:

1. The production of boot polishes and creams, and of furniture and floor polishes. These are made up with white spirit and various waxes as a basis.
2. The manufacture of floorcloth and linoleum, where white spirit is incorporated in the paints used in this industry.
3. The production of metal polishes and polishing pastes, which consist essentially of mixtures of white spirit with abrasive earths.

PETROLEUM AS A SOURCE OF LACQUER SOLVENTS

By **THOS. H. DURRANS**, D.Sc. (Lond.), F.I.C.

A. Boake Roberts & Company, Ltd.

PETROLEUM hydrocarbons do not dissolve cellulose acetate or nitrate which form the basis of 'cellulose lacquers', and the direct use of hydrocarbons in lacquers is limited to that of diluents added mainly for the purpose of reducing the cost of the lacquer; but in petroleum we have a raw material from which can be and are made a wide variety of solvents used regularly in the manufacture of lacquers; indeed it is quite possible that petroleum may in time to come be the sole ultimate raw material from which industrial organic solvents will be made.

The solvents made from petroleum may be placed into two classes, those arising from 'straight fractions' and those from the gaseous by-products of cracking processes, the former being saturated paraffins and the latter olefines.

From the saturated paraffins we get certain chloro-paraffins such as methylene dichloride and carbon tetrachloride and also amyl alcohols and their esters, while the olefines serve as raw materials for other chloro-hydrocarbons, a wide range of aliphatic alcohols and their esters and ethers—also acetone and homologous ketones and their products.

The production of chlorinated derivatives from petroleum is described elsewhere in contributions by H. B. Haas ('The Chlorination of Methane and its Homologues'; 'The Addition of Halogens to Olefine Bonds') and will not be reviewed here.

Aliphatic Alcohols and Acetates

The manufacture of aliphatic alcohols from petroleum has been accomplished for a number of years, mainly from the olefines produced by the cracking of petroleum.

The gases resulting from the pyrogenic decomposition of petroleum vary in composition according to the material, process, and apparatus used: in general they consist mainly of hydrogen, carbon monoxide and dioxide, methane and higher paraffins, ethylene, propylene, butylenes, higher olefines, and dienes. High-temperature vapour-phase cracking methods yield gases relatively rich in olefines with ethylene preponderating. Cracking temperatures of 600–650° C. normally lead to gases containing upwards of 50% of unsaturated hydrocarbons of which about one-half is ethylene and 5 to 9% butylene. Low-temperature liquid-phase cracking methods yield propylene as the main olefine in quantity up to 10% of the gases, while ethylene is present to the extent of about 5% and butylene 4%.

These gases serve as raw material from which are manufactured ethyl alcohol, iso-propyl alcohol, *sec.*- or *tert.*-butyl alcohols, and isomeric amyl alcohols. The industrial process consists essentially in absorbing the olefines in sulphuric acid and subsequently hydrolysing the alkyl sulphates. The preliminary separation of the olefines one from another is not customary, but can be effected by liquefaction with cold and under pressure followed by fractional distillation [4]. Normally the process consists in progressively treating the dried gases with sulphuric acid of progressively increasing concentration and under varying conditions of temperature. One method [5] is a continuous process in which the gases are treated serially in a system of towers, first with 80% sulphuric acid to remove the higher olefines more reactive than propylene such as diolefines and amylenes, then retreatment with 90% sulphuric acid at a temperature below 20° C. It is possible to effect almost quantitative separations of the various olefines by appropriate treatment—thus at 30° C. sulphuric acid of 66% strength absorbs iso-butylene almost exclusively, 85% acid absorbs α- and β-butylenes, 94% acid absorbs propylene, while 98% acid at 100° C. is required for ethylene: the yields of alcohols which can be obtained are 100% of the theoretical of *tert.*-butyl alcohol from iso-butylene, 80% of *sec.*-butyl alcohol from β- and β-butylenes, 90% of iso-propyl alcohol from propylene.

It has also been proposed to absorb the olefines under pressure in a solvent oil, such as the liquid paraffin, and then to dissolve the olefines selectively with the appropriate strengths of acid either batch-wise or by a continuous process [40].

The absorption of ethylene in sulphuric acid was found by Sidgwick and Plant in 1919 to lead to the formation of not only ethyl hydrogen sulphate but also to diethyl sulphate [34, 1919, 1921], by conducting the process under pressure the yield of diethyl sulphate can be increased [27] while the rate of reaction may be accelerated by the use of copper, iron, and silver catalysts [16, 1922, 1924]. The diethyl sulphate which is formed in this manner separates out of the reaction mixture and may be removed, and in this manner the proportion of ethylene which can be absorbed in a given quantity of sulphuric acid is considerably increased with consequent advantage in the recovery process subsequent to the hydrolysis to alcohol.

Propylene is more easily absorbed than ethylene by sulphuric acid, and for this reason weaker acid and lower temperatures may be used, thus avoiding the formation of polymers which result from treatment with strong acid, such as, for instance, 98% acid at 25° C. which leads to the immediate formation of a mixture of saturated and diolefinic open chain polymers.

The ease with which olefines react with sulphuric acid to form sulphuric esters attains, in general, a maximum with the amylenes and hexylenes: of the butylenes the iso-butylene is much the most reactive, being soluble in 17% acid. Propylene and α-butylene dissolve at about the same rates in sulphuric acid of any given concentration, while β-butylene dissolves at about twice the rate and iso-butylene at a rate estimated at as much as 40 times as fast as α-butylene [25, 1930] at 25° C.

The factors which govern the rates of formation of the alkyl sulphates are the structure of the olefine, the strength and proportion of the acid, and the time of contact. The olefines may be divided into the three following groups [28, 1929]:

1. Those which dissolve readily in 60–70% sulphuric acid yielding tertiary alcohols on hydrolysis and which are easily polymerized by hot dilute acid or by concentrated acid, e.g. iso-butylene, tri-methyl ethylene, β-methyl α-butylene.
2. Those which are almost insoluble in sulphuric acid of

all concentrations which on hydrolysis yield no secondary alcohol and only a trace of tertiary alcohol and which polymerize more slowly than those of group 1, e.g. iso-propyl ethylene.

3. Those which dissolve in 75–85% sulphuric acid yielding secondary alcohols on hydrolysis and which are much more resistant to polymerization than those of the other groups, e.g. α-butylene, β-butylene, α-amylene, and β-amylene.

The reactivity of the amylenes decreases in the following order [29, 1927]:

1. Tri-methyl ethylene.
2. β-methyl α-butylene.
3. β-amylene.
4. α-amylene.
5. Iso-propyl ethylene.

The olefines 1 and 2 react much more readily than 3 and 4 while 5 polymerizes without forming sulphate. α- and β-amylenes can be readily converted into secondary alcohols by shaking with equal volumes of 84% sulphuric acid, diluting the solution with 8 vols. of water, and distilling.

Generally with increase of molecular weight from ethylene to the amylenes greater reactivity with sulphuric acid is shown, diminishing with further increase in molecular weight. The stronger the acid and the higher the temperature the greater the tendency to polymerization. The iso-olefines which yield tertiary alcohols are the most reactive in the descending order: iso-butylene, tri-methyl ethylene, β-methyl α-butylene, followed by iso-propyl ethylene, β-butylene, α-butylene, β-amylene, α-amylene, propylene, ethylene. The conversion of the sulphuric esters of those olefines which yield secondary alcohols can be effected by dilution with water and steam distillation, but those yielding tertiary alcohols must be neutralized beforehand.

In order to prevent or minimize the formation of polymers attempts have been made to accelerate the rate of formation of the sulphates by means of catalysts: silver and mercury salts were first tried with some success: a later method [6] consists in the use of catalysts prepared by adding ferrocyanides to strong sulphuric acid and treating the solution with an olefine of the type of group 3 to form a 'double compound' which is itself a catalyst for the hydration of olefines of all classes. Thus the double compound is formed with a hydrocarbon which does not readily polymerize and then used to catalyse the sulphate formation of normally readily polymerizable olefines.

Another method by which polymerization is restricted is to avoid the presence of excess of sulphuric acid [7]: thus dibutyl sulphate is formed by treating liquefied α- or β-butylene with an insufficiency of 90–100% sulphuric acid at normal temperature under pressure. On releasing the pressure the excess butylene distils off and the remaining sulphuric ester is converted to secondary butyl alcohol by diluting with water and heating: the process is also applicable to the formation of amyl and hexyl alcohols.

A similar process is used for the preparation of tertiary butyl alcohol from iso-butylene [8]; thus liquefied iso-butylene is shaken at low temperatures with an insufficiency of 65% sulphuric acid. The product is neutralized and distilled: yields of 85% of the theory of tertiary butyl alcohol can be obtained, the by-products being di-iso-butylene and tri-iso-butylene. Similarly, tertiary amyl alcohol can be prepared from mixtures containing tri-methyl ethylene and β-methyl α-butylene by treating the liquefied olefines at temperatures below 20° C. with 65% sulphuric acid neutralizing with lime and distilling.

A further method for preparing *sec.*- and *tert.*-butyl alcohol consists in absorbing the butylenes in liquid paraffins under pressure, treating the solution at normal temperatures first with 65% acid whereby *tert.*-butyl hydrogen sulphate is formed and thereafter with 70% acid at 40° C. to form *sec.*- and iso-butyl hydrogen sulphates which are then hydrolysed.

An interesting step in the preparation of *sec.*-butyl alcohol is that of polymerizing ethylene to β-butylene [9] by passing liquefied ethylene with 2% of borom fluoride at 60 atm. pressure over a nickel catalyst at 8–10° C.

The alcohols which can be prepared from olefines by the sulphuric acid method comprise ethyl alcohol, iso-propyl alcohol, *sec.*-butyl alcohol, *tert.*-butyl alcohol, methyl-propyl carbinol, methyl iso-propyl carbinol, *tert.*-amyl alcohol, methyl-butyl carbinol, methyl iso-butyl carbinol. The alcohols with the exception of ethyl are all secondary or tertiary alcohols, but the conversion of ethyl alcohol to *n*-butyl alcohol has also been accomplished industrially by a four-stage process involving first the dehydrogenation or oxidation of ethyl alcohol to acetaldehyde, the polymerization of this to aldol, followed by dehydration to crotonaldehyde and hydrogenation to *n*-butyl alcohol. The direct one-stage conversion of ethyl alcohol to *n*-butyl alcohol has also been recorded [10]. If ethyl alcohol be passed over barium oxide at 400–450° C., a considerable portion is converted to *n*-butyl and higher alcohols together with ethyl acetate, acetal, acetone, and acetaldehyde: by introducing hydrogen into the system with a catalyst of magnesium oxide promoted with heavy metal oxides the formation of aldehyde and acetone is suppressed, but increasing proportions of hydrogen is accompanied by an increase in the proportion of higher alcohols. Mixtures of ethylene and alcohol can also be used in this process.

Another method for the preparation of alcohols from olefines which has been much studied during recent years consists in the treatment of olefines and steam with catalysts such as silver nitrate, cuprous chloride, mercuric chloride [36, 1928], boron phosphate [20, 1931], and many other catalysts [35, 1928, 1930–4]. By this means ethyl and iso-propyl alcohols have been prepared: the degree of conversion is, however, but small.

The widespread use of ethyl alcohol needs no comment: the other alcohols arising from petroleum do not find very extensive use as solvents, but they serve as raw materials for the preparation of solvents for cellulose esters. Among the more important of these solvents are the acetates made by esterification of the alcohols. Some of these esters have, however, been made from olefines by direct methods not involving the isolation of the corresponding alcohol.

The direct preparation of ethyl acetate from ethylene and acetic acid [33, 1919] has been effected but has proved to be very difficult to accomplish—indeed, the process has been used to separate ethylene from propylene which esterifies more readily [41, 1930]. By treating equal volumes of sulphuric acid and acetic acid at 40° C. with propylene until absorption ceases a yield of 80% on the propylene may be obtained of a mixture of iso-propyl alcohol and acetate [42, 1930]—combination may also be effected by passing the mixed vapours of propylene and acetic acid over absorbent charcoal saturated with a dehydrating catalyst [38, 1933].

The method by which iso-propyl acetate is manufactured in bulk is that of saturating sulphuric acid with propylene in the presence of a hydrocarbon oil and gradually adding calcium acetate at 70–90° C.: the hydrocarbon oil absorbs the ester as it is formed and after careful neutralization the ester is separated by distillation.

The direct preparation of *sec.*-butyl acetate from α-and β-butylene has been accomplished by heating a mixture of the olefine with acetic and sulphuric acids in the presence of ferrocyanides [30, 1925], a yield of 70% of *sec.*-butyl acetate being obtained.

Another method consists in passing a mixture of acetic and sulphuric acids down a tower up which the liquefied olefine is passing at 150 lb. pressure and at 750° C. Further, the liquefied olefine treated with a mixture of 4 vols. of acetic and 1 of sulphuric acid gives a conversion to butyl acetate of 52% calculated on the acetic acid, with but 3% of polymerized olefine [19]. Amylene and acetic acid react at normal temperatures in the presence of zinc chloride with the formation of a secondary amyl acetate and polymerized olefine. Very little information seems to exist on this subject.

In general the higher aliphatic olefines react more readily with organic acids than do the lower homologues. *Sec.*-octyl acetate can be made by heating α- or β-octylene with acetic acid at 300° C. under pressure, while heptylenes similarly yield *sec.*-heptylacetate.

Another quite different route by which aliphatic alcohols and esters can be made is that from the saturated paraffins; this has been applied industrially to the large-scale manufacture of the isomeric amyl alcohols and their acetates [15, 1927, 1930]. A fraction of petroleum consisting of a mixture of *n*- and iso-pentane is chlorinated to about 25% of the theory for a mono-chloro-pentane, in the vapour phase under carefully controlled conditions to prevent explosive combination. After removal of the hydrochloric acid which is simultaneously produced, the amyl-mono chlorides are isolated by distillation and a product of the following approximate composition obtained:

	%
1-chloro-pentane	26
2- ,, ,, ...	18
3- ,, ,, ...	8
2-methyl 4-chloro-butane .	16
2- ,, 2- ,, ,, .	32

The amyl alcohols are produced from this mixture by hydrolysis under pressure with sodium hydroxide in the presence of sodium oleate—the product is fractionally distilled to separate *tert.*-amyl alcohol, diamyl ether, and unreacted amyl chlorides from the main amyl alcohol fraction which consists of a mixture of *n*-amyl alcohol, methyl propyl carbinol, diethyl carbinol a sym.-amyl alcohol and iso-amyl alcohol, known industrially as Pentasol. The isolation of these alcohols from one another is not an economic industrial operation, although it has been accomplished.

The acetates are produced in a similar manner from the amyl/chlorides by heating under pressure at 200–230° C. with a mixture of powdered sodium acetate and carbon.

Aliphatic Ketones

Ethyl alcohol, iso-propyl alcohol, and the secondary alcohols which result from the hydration of olefines serve as raw materials for the manufacture of ketones, some of which find very wide industrial use as solvents, in particular acetone, and, to a less extent, methyl-ethyl ketone.

The chief problem involved in this conversion is that of suppressing the simultaneous reformation of olefines by dehydration; until recently the results had not been satisfactory, but yields close to those theoretically possible have now been obtained industrially by means of special catalysts.

The industrial manufacture of acetone is accomplished in several ways, but of interest here are two methods which are related to petroleum as the original raw material, the route being either through ethyl alcohol or through iso-propyl alcohol.

The production of acetone from ethyl alcohol is effected by passing steam carrying about 10% of alcohol at 500° C. over catalysts consisting of the oxides of the so-called 'heavy metals' such as iron, manganese, and copper promoted with oxides of calcium and magnesium [11]: 2 molecules of alcohol and 1 of water react to produce 1 each of acetone, carbon dioxide, and 4 of hydrogen: the reaction is endothermic and probably takes place in two stages involving first the formation of a metallic acetate and hydrogen followed by the breakdown of the acetate into acetone and carbon dioxide. The yield of acetone is about 80% of the theory: this yield may be improved by operating under diminished pressure and also by promoting the iron oxide catalyst with oxides of nickel, cobalt, and chromium when the yield increases to over 90%. Another variation [17] consists in forming barium acetate by passing ethyl alcohol over barium oxide and then decomposing this at a higher temperature. The greater part of the acetone produced in this country is made by methods similar to those described above, but in the United States of America it is mainly produced by fermentation methods from carbohydrates and by the dehydrogenation and oxidation of iso-propyl alcohol obtained by hydrating the propylene resulting from petroleum cracking processes. The dehydrogenation of iso-propyl alcohol is effected by heating with various catalysts such as nickel, platinum, copper, cobalt, manganese, and brass, but among the most successful methods is that of passing iso-propyl alcohol with or without water through molten lead or molten mixtures of the chloride of calcium, barium, magnesium, or potassium at about 625° C. Yields up to 95% are obtainable. The oxidation of iso-propyl alcohol to acetone is effected by means of metal or metallic oxide catalysts such as are used for the dehydrogenation process, but in this process air is admitted with the acetone and this procedure has the effect of changing the endothermic dehydrogenation into an exothermic oxidation; by the careful control of the proportion of air the process can be made self-supporting as regards heat consumption.

Secondary butyl alcohol can be converted to methyl-ethyl ketone by means of catalysts consisting of alloys of copper and zinc, the yield rising as high as 96% at 346–480° C. At this higher temperature dehydration of the alcohol to butylene begins: at 600° C. the product contains about 8% of butylene, while still higher temperature causes the formation of carbon which fouls the catalyst and chokes the plant. Another efficient catalyst much favoured for reactions of this type and particularly for the production of acetone is zinc chromate promoted with sodium carbonate—this catalyst is very robust and leads to yields of 90% or more when the degree of conversion is 30–40% of the alcohol passed.

Acetone can also be obtained by passing ethyl acetate over a calcium-oxide catalyst at 400–500° C. The reaction involves first the formation of acetone and alcohol followed by the conversion of the alcohol to acetone—thus the whole of the ester is converted to acetone, the yield being about 85% of the theory.

A new method for the production of ketones is the combination of tertiary hydrocarbons of the type CHR_3 with carbon monoxide by means of aluminium halide catalysts at low temperatures: thus iso-pentane with carbon monoxide yields a hexanone probably 3-methyl pentanone 2.

The use of iso-propyl alcohol as an intermediate for the synthesis of esters is likely to be of great importance if yields can be improved. The pyrolysis of iso-propyl alcohol or its dehydrogenation product, acetone, by passage over copper or through molten lead at 700–750° C. leads to the production of ketene in yields of about 38% on the acetone consumed, together with about 46% of methane and 16% of carbon monoxide and ethylene. Ketene is a very highly reactive substance and may be regarded as the ultimate dehydration product of acetic acid, acetic anhydride being the half-way dehydration product. Ketene is therefore a very powerful acetylating agent since water is not produced when acetylation is effected with it. The use of ketene as an acetylating agent has necessitated the development of a special technique by reason of its great tendency to polymerize. In order to prevent polymerization the ketene must be immediately diluted with a non-reacting substance or immediately reacted with the substance it is desired to acetylate. Acetone has been used as a non-reacting diluent, the dilution being effected by passing an excessive proportion of acetone through the pyrolysing apparatus or by passing the products of pyrolysis as quickly as possible into a tower down which acetone is passing. The ketene solutions thus produced are not entirely suitable for subsequent use as an acetylating agent, but it has been found possible to introduce the ketene, under suitable control, directly into the medium it is desired to acetylate, such as water, alcohols, glycols, and amines: by this means acetic acid, acetic anhydride, and acetates of alcohols and amines may be produced from acetone without the production of any water of reaction and without the use of any esterification catalyst, advantages of considerable technical significance. Incidentally it should be noted that in ketene we have one of the very few reagents by means of which the tertiary aliphatic alcohols may be acetylated.

From the various processes already described it will be seen that it is possible to synthesize ethyl acetate from petroleum: thus hydrating the olefines from cracked petroleum gives rise to ethyl and iso-propyl alcohols—from the latter ketene can be produced by way of acetone and the reaction between alcohol and ketene yields ethyl acetate.

The direct production from petroleum of a solvent containing a large proportion of esters has been investigated by James for a number of years. James passed selected fractions of petroleum with air over catalyst such as the blue oxides of molybdennum at 200–500° C. and under ordinary pressure: the product, which besides unchanged petroleum consists largely of aldehydes, ketones, ethers, esters, and organic acids, is extracted with alcohol and the alcoholic extract treated with hydrochloric acid gas which causes the organic acids and aldehydes to combine with the alcohol to form esters and acetals. The resulting mixture consisting mainly of esters, acetals, ketones, and ethers is, after purification, separated into a low-boiling solvent for cellulose nitrate and a plasticizer.

Glycol Ethers

One of the most important directions in which petroleum has been used for the production of cellulose-ester solvents is that which leads to the glycol ethers: of these the mono-ethyl ether of ethylene glycol, known otherwise as ethyl glycol or as ethoxy ethanol and industrially as Cellosolve, has reached an output approaching that of butyl acetate.

The starting-point for this industrial synthesis is ethylene, which is first converted into ethylene chlorhydrine (2-chlorethyl alcohol) by treatment with water and chlorine [26] or with chlorine and aqueous caustic alkali [14, 1924]. The process involving the use of the latter is conducted in a closed vessel filled with 6% caustic soda solution treated with the equivalent quantity of chlorine and ethylene, being then passed through the sodium hypochlorite solution thus formed: as the reaction proceeds, part of the solution is withdrawn and replaced with fresh reactants in a continuous manner. The solution contains about 10% of ethylene chlorhydrine which can be isolated by fractional distillation as a constant boiling mixture with water containing 42% of the chlorhydrine.

The earlier process for preparing the ethyl glycol consisted in first hydrolysing the chlorhydrine to glycol by passing the constant boiling mixture in vapour form up a tower down which is falling a solution of sodium carbonate: hydrolysis takes place and the glycol dissolved in the solution of sodium chloride passes to the bottom of the tower, while carbon dioxide, acetaldehyde, and steam pass away at the top. The glycol is isolated by evaporation of the solution, separation of the sodium chloride, and fractional distillation, and is then treated with di-ethyl sulphate and alkali to form the mono-ethyl ether [40].

This process, which is also applicable to the manufacture of other glycol ethers, such as butylene glycol ethers, has been replaced by one involving the formation of ethylene oxide, but the advent of very cheap diethyl sulphate may cause reversion to the earlier method. The ethylene oxide method consists firstly in the preparation of the oxide by passing the chlorhydrine at high temperatures over solid bases or through suspensions of lime or soda-lime in water [12, 1921, 1924] or by treating solutions of the chlorhydrine at 30–60° C. with 30% caustic soda solution [1, 1931], or directly from ethylene by treating this under pressure with air and steam at 150–400° C. in the presence of catalysts such as silver [37, 1931]. The next step in the process is to combine ethylene oxide with ethyl alcohol, using small quantities of catalysts such as sulphuric acid [24] or diethyl sulphate [2] at 100° C. and under a pressure of 3–4 atm., yields being of the order of 90–5%: other catalysts are zinc, nickel, or chromium sulphates [21, 1928]; aluminium hydrosilicates [22, 1930] using 5% of the last-named catalyst having a *pH* of about 2,3-yields of 80% are obtainable by passing ethylene oxide into alcohol at 80° C.

By substituting other olefine oxides for ethylene oxide or other alcohols for ethyl alcohol, various homologous glycol ethers can be prepared, such as butyl glycol and butylene glycol ethyl ether.

Ethylene oxide has also been used industrially for preparing the ring ether, dioxane, or 1,4-diethylene oxide by heating with sodium hydroxide [23, 1924, 1927]. Dioxane has also been prepared by treating 1,4-dichlorethyl ether with strong bases—thus 5% aqueous caustic soda at 200° C. leads to the formation of dioxane in 90% yield of the theory—the dichlorethyl ether is obtained by treating glycol chlorhydrine with sulphuric acid. Dioxane is a dangerously toxic solvent [3]. Other oxides of this class can similarly be prepared by treating the appropriate dichloro-olefine with metallic oxides such as litharge, whereby ring closure is effected: thus dimethyl dioxane results from β,β'-dichloro-dipropyl ether and methylene ethylene oxide from chlormethyl-chlorethyl ether.

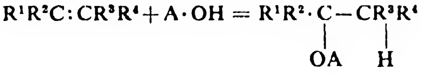
Aliphatic Ethers

The production of diethyl and other ethers by the action of sulphuric acid or other dehydrating catalysts on alcohols needs no comment—other methods of production are, however, of interest.

The ease with which olefinic hydrocarbons can be made to yield alkyl sulphates by the direct absorption in sulphuric acid would lead to the supposition that this method would be adaptable to the production of the corresponding ethers. It is significant, however, that although Fritsche used the process in the laboratory as long ago as 1896, when he prepared diethyl ether from ethylene [18, 1896], no large-scale use of the process seems to be recorded beyond that tried and abandoned at Skinningrove in 1920 [13].

The direct production of ethyl ether by contact catalysis from ethylene and steam has also been noticed in processes of that type for the production of alcohol, while the preparation of aliphatic ethers from the alcohols by passage over aluminium oxide was first recorded in 1901 by Grigoreff: the method has been developed by Sabatier and his colleague and yields of 98–100% obtained by passing alcohol vapour over specially prepared oxides of thallium, aluminium, and tungsten at 340–350° C.: the same procedure, however, leads to bad yields from higher alcohols. An industrial method [31, 1929] developed about 1929 consists in passing alcohols over aluminium or chromium sulphate at temperatures not exceeding 300° C. and at high pressure: by this means *n*-butyl alcohol may be converted to di-*n*-butyl ether at 45% conversion and with yields approaching 100%.

Certain so-called 'tertiary' ethers have been made by the combination of olefines and alcohols in the presence of condensing agents such as sulphuric acid [32] in the manner indicated by the following general equation:



$$R^1R^2C{:}CR^3R^4 + A{\cdot}OH = R^1R^2{\cdot}\underset{OA}{C}-\underset{H}{C}R^3R^4$$

Among the ethers thus produced are methyl and ethyl tertiary butyl and tertiary amyl ethers.

REFERENCES

1. Anglo-Persian Oil Co. B.P. 374,864 (1931).
2. —— B.P. 367,353.
3. Ass. Brit. Chem. Mnfrs. Safety Circulars nos. 65 and 76.
4. B.P. 303,176; U.S.P. 1,879,660.
5. B.P. 249,834.
6. B.P.s 323,748, 381,723.
7. B.P.s 377,583, 376,925; U.S.P. 1,854,581.
8. B.P. 360,331.
9. B.P.s 293,487, 313,067, 326,322.
10. B.P. 282,448.
11. B.P. 359,430.
12. Burdick, J. N. B.P. 236,379 (1924); G.P. 403,643 (1921).
13. Bury, E. B.P. 147,360.
14. Carbide and Carbon Chemicals Co. B.P. 235,044 (1924).
15. Clark, L. H. *Ind. Eng. Chem.* **22,** 439 (1930); Koch, G. T., and Burrell, G. A. *Ind. Eng. Chem.* **19,** 442 (1927).
16. Damiens, A. *Compt. rend.* **175,** 585 (1922).
    Gludd, W., and Schneider, G. *Ber.* **57** B, 254 (1924).
17. Dreyfus, H. B.P. 345,271.
18. Fritzsche, P. B.P. 20,225 (1896).
19. Frolich, P. K., and Young, F. L. U.S.P. 1,877,291.
20. Horsley, G. F. B.P. 378,865 (1931).
21. I.C.I. B.P. 322,037 (1928).
22. I.G. B.P. 354,357 (1930).
23. —— G.P.s 500,223 (1924), 516,844 (1927).
24. —— B.P. 271,169.
25. *J.A.C.S.* **52,** 721 (1930).
26. Kerfoot, T., Kerfoot, E., Irvine, J., and Haworth, W. B.P. 128,625 (1917).
27. Maimerie, C., ass^r to Legoda, S. A. B.P. 215,000 (1923).
28. Norris, J. F., and Davis, H. S. *J.S.C.I.* 71 (1929).
29. Norris, J. F., and Joubert, J. M. *J.A.C.S.* 873 (1927).
30. N. V. Bataafsche Petroleum. B.P. 235,547 (1925); *J.S.C.I.* 738 (1925).
31. —— B.P. 332,756 (1929).
32. —— B.P. 393,753; U.S.P. 1,968,601.
33. Oehme. G.P. 372,717 (1919).
34. Sidgwick, N. V., and Plant., S. G. P. B.P. 157,578 (1919); *J.S.C.I.* **40,** 14 T (1921).
35. Slade, E. B.P. 308,859 (1928).
    N. V. Bataafsche Petroleum. B.P. 335,551 (1930).
    Joshua, W. P., Stanley, H. M., and Dymock, J. B. B.P. 368,051 (1931), 392,289 (1932), 392,685 (1933), 408,932 (1933), 415,426 (1934), 415,427 (1934).
    Horsley, G. F. B.P. 369,216 (1931).
36. Smith, H. G., and Bridgen. B.P. 308,468 (1928).
37. Soc. Française Catalyser Genl. B.P. 402,435 (1931).
38. Strange, E. H., and Kane, T. B.P. 398,527 (1933).
39. U.S.P. 1,614,883.
40. U.S.P. 1,365,043.
41. Woolcock, I. W. B.P. 334,221 (1930).
42. —— B.P. 334,228 (1930).

SELECTED BIBLIOGRAPHY

Brooks, B. T. *The Non-benzenoid Hydrocarbons* (Chemical Catalogue Co., 1922).

Durrans, T. H. *Solvents*, 3rd ed. (Chapman & Hall, Ltd., 1933).

Ellis, C. *The Chemistry of Petroleum Derivatives* (Chemical Catalogue Co., 1934).

KEROSINE

By J. KEWLEY, M.A., F.I.C., M.I.Chem.E., M.Inst.P.T., *Chief Chemist*, and C. L. GILBERT, A.R.C.S., B.Sc., M.Inst.P.T., *Anglo-Saxon and Asiatic Petroleum Companies, Ltd.*

Introduction

THE word 'lamp' is derived from the Greek λαμπας 'a torch', which connotes the earliest source of artificial light available to primitive man. The first step in development must have been associated with the endeavour to utilize as illuminants the vegetable and animal oils and fats then available. Archaeological explorations have revealed that the Egyptian and other ancient peoples used wick-fed lamps many thousands of years ago. From the earliest times down to the present day lamps have played an important part in ceremonial observances, while they were not unknown to mythology, as evidenced by the story of Psyche inadvertently letting a drop of hot oil from her lamp fall on the sleeping Cupid.

It was not until the middle of the eighteenth century that attempts were made to produce oils by distillation of coals or shales. Selligue in France as early as 1840 made, and purified to some extent, an oil by the distillation of shale, which oil was extensively sold in Europe. About 1846 Abraham Gesner successfully manufactured distillate oils from coal and used them for burning in lamps. His patents were sold to the North American Gas Light Company, and the oils were manufactured and sold under the denomination of **Kerosene Oil** (from κηρος wax and ἔλαιον oil). The name thus originated as the trade name of a private firm. International agreement has now decreed that it be spelt **Kerosine.** International agreement has, however, not yet succeeded in eliminating the names or rather misnomers by which it is still known, as, for example, 'paraffin oil' in Great Britain. In 1848 James Young of Glasgow made a kerosine by the distillation of crude petroleum from a seepage in a coal mine in Derbyshire, England, and subsequently made it on a commercial scale from a cannel coal in Scotland. This proved such a success that by 1860 no less than 40 works on the American Atlantic border were busy producing about 1,000 tons of illuminating oil per annum from cannel coal imported from Great Britain for the purpose.

The demand for a satisfactory illuminant was the stimulus which initiated the search for petroleum and was the chief factor which determined the rapid growth of the industry. Within ten years from the bringing in of Drake's well, Pennsylvania was producing two million barrels of crude oil per year. The coal oil works closed down and the distillation of cannel coal ceased and so far has never been revived. A few years later kerosine was to be found in use in the remotest parts of the world, and for the next forty years continued to be the mainstay of the industry.

The efforts of the refiners were therefore mainly directed to producing from the crude the maximum quantity of this product, only too often with little regard to the quality. The incorporation into the kerosine of as much as possible of the then valueless gasoline fractions resulted in the production of such highly inflammable oils that, in consequence of the large number of fatal accidents resulting from its use, it acquired at one time in the United States the unenviable name of 'domestic dynamite'. Legislation in various countries soon curbed the activities of the oil refiner in this direction and resulted in the introduction of inflammability limits based on fire tests or flash-points, so that kerosine became a safe product with a flash-point of over 73° F. (23° C.). Subsequently the increasing demands for gasoline brought about a reduction in the volatile components of the kerosine, and a much higher flash-point.

Such changes in the relative demands for other petroleum products, together with the introduction of gas and electric lighting, have so greatly reduced the percentage of kerosine extracted from the crude that this once all-important product now occupies a position of relative insignificance, as is well illustrated by the following figures:

TABLE I

Year	*Percentage yield of kerosine from crude oil, U.S.A.*	*Actual production U.S.A. (figures bbl.* $\times 10^6$*)*
1899	57·6	33
1904	48·3	57
1909	33·0	60
1914	24·1	63
1919	15·4	55
1924	9·3	57
1929	5·8	53
1934	5·9	53·5
1935	5·8	55·8

The total world consumption of kerosine for 1936 was 17,350,000 metric tons.

The diminished yield of kerosine from the crude oil is, however, due not only to the narrowing of the distillation range, but also to the fact that as new fields were opened up, crudes containing a large content of good kerosine became relatively scarcer. The types of lamp first established on the market were designed to burn well only oils from crudes of the paraffin type. As other crudes relatively rich in naphthenic and even aromatic hydrocarbons appeared on the scene, the unsuitability of the lamps either excluded certain types of kerosine altogether, or made it necessary to give them such heavy chemical treatments that they lost considerable percentages of their bulk in the process.

The introduction of the kerosine-burning internal combustion engine has provided a new outlet, and the use in the U.S.A. of stove and light burner oils in character almost heavy kerosines, has brought about a considerable increase in consumption during the last few years. The appearance of more efficient burners and appliances for heating and cooking purposes utilizing kerosine as fuel, holds out further promise of a considerable increase in consumption.

General Characteristics

Although the properties of a product such as kerosine must be considered in relation to the apparatus in which, or the purpose for which it is used, certain general characteristics can be independently considered. No precise definition of kerosine is possible, as broadly speaking, it consists of those fractions of crude oil which are distilled off between the gasoline and gas oil ranges. Its boiling-point range is thus determined partly by the limits so imposed and partly by the demands of the market for grades for various purposes.

In most countries two types of kerosine are marketed, the one for use in lamps, heaters, and cookers, the other for use as fuel for internal combustion engines (power kerosine). The great diversity in the characteristics of kerosines sold for these two purposes in different countries is illustrated by the data given in Table II.

TABLE II

Refined Kerosines on the World Markets

Specific gravity at 15/4° C.	* A.S.T.M. distillation: Initial boiling-point ° C.	Percentage distilling to 200° C. %	Final boiling-point ° C.	Sulphur content %	Aromatic content %	Smoke-point (I.P.T.)†
Illuminating Kerosines						
1. 0·786	176	19	268	0·03	4	41
2. 0·787	165	30	272	0·06	6	39
3. 0·796	165	35	277	0·08	7	33
4. 0·804	170	26	264	0·02	5	30
5. 0·793	168	38	270	0·11	21	27
6. 0·801	165	36	271	0·06	14	26
7. 0·809	163	24	300	0·04	11	25
8. 0·809	180	10	287	0·02	12	25
9. 0·806	174	19	260	0·04	19	24
10. 0·796	150	70	243	0·14	21	23
11. 0·805	170	20	270	0·13	17	23
12. 0·805	169	31	270	0·03	17	23
13. 0·835	153	70	235	0·03	18	22
14. 0·821	149	45	289	0·05	16	22
15. 0·809	128	37	274	0·04	19	21
16. 0·818	172	11	281	0·04	18	21
17. 0·826	178	29	269	0·06	15	21
18. 0·815	161	30	291	0·03	22	21
19. 0·829	195	1	280	0·20	21	20
20. 0·811	137	45	290	0·04	18	20
21. 0·847	170	25	263	0·04	40	12
Power Kerosines						
1. 0·837	140	54	260	0·28	50	..
2. 0·835	152	73	237	0·04	18	..
3. 0·817	154	57	270	0·04	27	..
4. 0·845	140	60	255	0·05	55	..
5. 0·805	101	73	233	0·05	30	..
6. 0·827	143	72	236	0·09	36	..
7. 0·813	137	52	232	0·02	16	..
8. 0·825	140	72	232	0·18	35	..

* American Society for Testing Materials.
† Institution of Petroleum Technologists.

It is apparent that there are wide variations in the properties of the illuminating oils dependent on (*a*) market requirements, (*b*) the type of crude from which they are made, and (*c*) the type of chemical treatment given.

(*a*) Any one market must be supplied with a type or types of kerosine to suit the lamps in general use, which may range from the simplest home-made lamp to the most efficient types.

(*b*) The kerosine distillates in general display the characters of the crudes from which they are directly derived. For example, a paraffin base crude will yield a kerosine in which the paraffin hydrocarbons predominate, while if the sulphur content of the crude oil is high, that of the kerosine distillate will also be high, though this may be adjusted by subsequent refining.

(*c*) The chemical treatment given may be devised either to remove small quantities of unwanted components or to alter fundamentally the character of the oil by the removal of a certain class of hydrocarbon.

The power kerosines differ widely in type from the illuminating kerosines as the requirements of the engine and of the lamps differ so widely. This is discussed in more detail later (*vide* p. 2483).

Chemical Composition

Kerosine distillates consist in the main of hydrocarbons, but usually contain as impurities compounds containing sulphur, nitrogen, and oxygen.

(*a*) **Hydrocarbons.** The main types of hydrocarbons present in kerosine are usually roughly classified as paraffins, naphthenes, and aromatics. Their great complexity makes more accurate definition impossible in the light of present knowledge. For the purposes of this discussion paraffins and naphthenes are used in the generally accepted sense, while aromatics are considered as those hydrocarbons which can be removed by treatment with 98% sulphuric acid. Very rarely are hydrocarbons of any one of these series entirely absent, except in the case of oils specially treated by removing the aromatics. In general, kerosine distillates may contain up to 40% of aromatic hydrocarbons dependent on the chemical nature of the crude oil. Treatment by the Edeleanu process (*vide* p. 1888) is frequently given to reduce the content of aromatic hydrocarbons to a low figure. The relative preponderance of naphthene and paraffin hydrocarbons in kerosine distillate will depend on the chemical nature of the mother crude oil and is usually not appreciably altered by the present methods of chemical treatment.

Owing to the great complexity of the hydrocarbons in the kerosine boiling-range, comparatively little work has been done on the isolation of pure individuals. Rossini [45, 1935] of the U.S. Bureau of Standards, working on project no. 6 of the American Petroleum Institute, has isolated from the fraction of a Mid-Continent distillate boiling between 145° C. and 180° C., *n*-nonane, *n*-decane, mesitylene, pseudocumene, and hemimellitene, and found evidence also for the presence of propyl-benzene, ethyl-toluene, butyl-benzene, methyl-propyl-benzene, isomers of decane, and certain naphthenes. Birch and Norris [4, 1926], working on the acid sludge obtained by treating Iranian distillate with 20% of oleum, definitely identified aromatic hydrocarbons such as mesitylene, pseudocumene, hemimellitene, *p*-ethyl toluene, ethyl xylene, and a dimethyl-naphthalene. Mulany and Watson [37, 1924], working on Burma kerosine, found *p*-cymene. Mabery [26, 1900] isolated naphthalene from a California petroleum and Jones and Wootton [22, 1907] identified mono- and di-methyl derivatives of naphthalene in a Borneo petroleum. Tasaki and Yamamoto [51, 1931] isolated naphthalene, 2.methyl-naphthalene, and 2.6.di-methyl-naphthalene from the acid sludge of a Formosa kerosine. Even less work has been done on the non-aromatic hydrocarbons of the kerosine fractions. Unsaturated hydrocarbons are practically absent from kerosine distillates which have been prepared under non-cracking conditions.

Kerosines produced by cracking have so far not been used for illuminating purposes, but may find application as fuels for internal combustion engines. Such kerosines contain large percentages of unsaturated hydrocarbons of various types. No information as to the actual constitution of such hydrocarbons is as yet available.

The work referred to above is quoted merely as an indication of the complexity of the subject. In the present state of knowledge little would be gained by further discussion of this subject, as the relative effects of the various types of hydrocarbons present in a kerosine on its practical uses and applications can be so far only expressed in the light of the broad classification referred to above.

(*b*) **Sulphur Compounds.** Kerosine distillates may contain from 0·02% to 1·0% of sulphur in the form of a variety of organic compounds, many of which have been formed during distillation, and which may also subsequently be changed during acid refining of the kerosine. As a general rule, crude oils yielding as distillation residues large quantities of asphaltic bitumen give distillates of higher sulphur content than those of naphthenic or paraffin base types.

Much work has been done on the isolation, synthesis, and sulphur compounds occurring in crude oils, particularly in the benzine fraction [5, 1930], but comparatively little on those occurring in the kerosine fractions.

A number of sulphur compounds with boiling-points between 140° C. and 210° C. and which therefore may possibly occur in some kerosine distillates, have been synthesized. These belong to several types such as disulphides, thiophens, mercaptans, and thiocresols. In addition to these, hydrated thiophens or thiophanes (hexyl to octadecyl) have been isolated by Mabery and Quayle [29, 1906] from Canadian petroleum. Mabery and Smith [30, 1889] obtained indications of the presence of thioethers in the fractions boiling between 200 and 300° C. of an Ohio crude oil.

Sulphonic acids are also formed during the treatment of kerosine distillate with sulphuric acid, being found both in the oil and in the acid layer. Von Pilat, Sereda, and Szankowski [39, 1933] distinguish three classes, (1) the α-sulphonic acids, whose calcium salts are insoluble in water and ether, (2) the β-sulphonic acids whose calcium salts are insoluble in water but soluble in ether, and (3) the γ-sulphonic acids whose calcium salts are soluble in water but insoluble in ether. The sulphonic acids and their salts have been found of value in the manufacture of soaps and wetting agents. The difficulty in isolating sulphur compounds, particularly in view of their low yield from a kerosine distillate, is doubtless responsible for the lack of detailed information on the subject.

(*c*) **Nitrogen Compounds.** The nitrogen content of most crude oils is very small although Mabery [27, 1900] has found up to 2·35% in a Californian crude. E. J. Poth, W. D. Armstrong, C. C. Cogburn, and J. R. Bailey [40, 1928] consider that in general, little of the nitrogen is present in the crude oil in the form of bases, but that in distillates the bases appear along with non-basic nitrogen compounds of unknown structure. Mabery and Hudson [28, 1894] isolated several different bases from a Californian oil which they considered as derivatives of tetrahydro-pyridine and quinoline. Similar bases have been found in Galician, Roumanian, Russian, Japanese, &c., crude oils. The number of nitrogen compounds present in petroleum is certainly very large [23, 1930].

The question of the occurrence of nitrogen compounds in kerosine is of great interest in connexion with colour stability (*vide* p. 2473) on which subject much work has been done without, however, direct correlation with the actual nitrogen compounds present.

(*d*) **Acidic Bodies.** In addition to the sulphonic acids formed during acid refining of kerosine, other types of acids generally known as naphthenic acids occur in kerosine distillates. These are of three types: paraffin carboxylic, monocyclic, and bicyclic acids and occur in many crude oils, e.g. those from Russia, Roumania, Poland, Texas, California, Germany, and Japan. The content of such naphthenic acids varies from 0·1 to 2%.

The kerosine fractions yield naphthenic acids of higher acid value than do the gas-oil fractions, and these acids are more easily refined to a good colour.

Phenolic compounds have also been found in certain crude oils. Story and Snow [50, 1928] found small quantities of phenols in the distillates from mid-Continent crude and larger quantities in the cracked distillates.

With the exception of naphthenic acids, however, the non-hydrocarbon constituents of kerosines are at present of little or no practical importance, although their occurrence may throw some light on the question of the origin of crude oil.

Physical Properties

Certain physical characteristics are frequently determined as a check for consistency of refinery production, or for purposes of determining conformity to specifications; others are less frequently determined for specific purposes, such as for use in the design of plant or for some particular research. As various types of kerosine display such differences in their physical properties, the data published are so far from complete that only a brief summary is possible.

(*a*) **Specific Gravity.** The specific gravity of a kerosine is usually determined at 60° F./60° F. (American and British practice) or at 15° C./4° C. (Continental practice). It varies from about 0·775 to 0·850, although Edeleanu extract fractions of kerosine boiling-range may have specific gravities up to 0·885. A low specific gravity (below 0·800) often indicates an edeleanized kerosine, whereas a high-specific gravity (above 0·830) indicates a kerosine containing an unusually high percentage of aromatic or naphthenic hydrocarbons, or having an abnormal boiling-point range.

(*b*) **Distillation Range.** The distillation range of a kerosine is generally determined by the A.S.T.M. distillation method D. 86–35, and usually lies between 140 and 300° C. As will be seen from Table II (p. 2471) power kerosines have in general higher percentages distilling to 200° C. and lower final boiling-points than illuminating kerosines. Illuminating oils should not leave a dark-coloured residue in the flask after distillation as this indicates insufficient refining, and is generally accompanied by a high formation of char on the wick [35, 1933]. Within limits, the distilling range of an illuminating oil is only of indirect importance, i.e. in so far as it affects other properties, e.g. viscosity and flash-point, but with power kerosines the distillation range is a factor of direct importance.

(*c*) **Colour.** The colour of kerosine is generally determined in the Saybolt, Lovibond, or Stammer colorimeter. First-grade kerosines are expected to be water white, but for second-grade oils fashion is not so exacting. The colour however, gives no indication of the burning quality (*vide* p. 2474). Power kerosines, owing to the frequent addition of aromatic extracts are often discoloured.

(*d*) **Flash-point.** The Abel, Abel-Pensky, Pensky-Martens, Luchaire, and Tag (Tagliabue) instruments are in general use for determining the closed flash-point of kerosines, mainly to determine whether it meets Customs, &c., requirements in this respect, and as a check for contamination with gasoline. The 'fire-point' of kerosine, i.e. the temperature at which the oil will ignite in the open air under prescribed conditions, is still laid down in specifications in some parts of the world (e.g. U.S.A.).

(*e*) **Viscosity.** The viscosity of a kerosine is generally reported in absolute units, i.e. centipoises, being determined in instruments of the capillary tube type, e.g. the B.S.I. [6, 1929] or the Vogel Ossag viscometer [18, 1933]. The Saybolt Thermoviscometer and the Engler Ubbelohde viscometer are also used.

The value of the viscosity in assessing the burning quality of kerosine is discussed later (p. 2479).

(*f*) **Refractive Index.** The refractive index of a kerosine varies with the chemical composition for a definite boiling-point range: for a definite series of hydrocarbons the refractive index increases with the boiling-point.

Bacon and Hamor [1, 1916] give the following data:

TABLE III

Kerosine	*Specific gravity at 15° C.*	*Refractive index 15° C.*
American .	0·780	1·4345
Russian .	0·780	1·4309
Roumanian	0·780	1·4334
Galician .	0·780	1·4356
Shale . .	0·780	1·4373
American .	0·820	1·4564
Russian .	0·820	1·4533
Roumanian	0·820	1·4572
Galician .	0·820	1·4586
Shale . .	0·820	1·4568

(*g*) **Surface Tension.** The surface tension varies with the chemical composition of the kerosine, but little published data is available on this subject. Holde [17, 1924] gives the following figures for the surface tension against air of a kerosine of specific gravity 0·8467:

Temperature	*Surface tension Dynes/cm.*
0° C.	28·9
25° C.	26·4
50° C.	24·2

(*h*) **Specific Heat.** The specific heat of a kerosine at different temperatures varies with the specific gravity at 60/60° F. and is further affected by the chemical composition. The U.S. Bureau of Standards [53] gives the following figures:

TABLE IV

Specific gravity at 60/60° F.	*Specific heat at*					
	0° F.	*100° F.*	*200° F.*	*300° F.*	*400° F.*	*500° F.*
0·8251	0·427	0·477	0·526	0·576	0·625	0·675
0·7796	0·439	0·490	0·541	0·592	0·643	0·694

Oils from paraffin base crude generally give results 2% higher and those from naphthene base 2% lower than the above figures.

(*i*) **Calorific Value.** The following figures are given by Bacon and Hamor [2, 1916] and Redwood [44, 1922] for a number of various marketed kerosines:

TABLE V

Specific gravity (at 15° C.)	*Cal. per g.*	*B.Th.U. per imp. gal.*
	Gross values	
0·768	11,250	155,520
0·780	11,163	156,500
0·797	11,167	159,000
0·800	11,140	160,400
0·805	11,100	160,500
0·807	10,960	159,200
0·813	10,900	159,500
0·816	11,225	164,870
0·825	11,270	167,000

(*k*) **Latent Heat.** E. H. Leslie, J. C. Geniesse, T. W. Legatski, and L. H. Jagrowski [25, 1926] give the following data for the latent heat of vaporization of distillates from paraffin base crude, based on figures obtained on 1° F. cuts.

TABLE VI

Boiling-point	*Sp. gr. at 15/4° C.*	*Latent heat B.Th.U. per lb.*
300° F. = 149° C.	0·755	117·4
350° F. = 177° C.	0·775	109·0
400° F. = 204° C.	0·788	100·6
450° F. = 232° C.	0·808	92·2
500° F. = 260° C.	0·815	85·9
550° F. = 288° C.	0·822	75·5
600° F. = 315° C.	0·823	67·1

Bureau of Standards Misc. Pub. No. 97 (Thermal Properties of Petroleum Products) indicates that the latent heat of vaporization per unit volume at 60° F. of any petroleum oil is dependent only on the temperature of vaporization. The following relevant extracts are taken or interpolated from Table XV of this article:

TABLE VII

Temp. ° F.	*Latent heat of all petroleum oils of sp. gr. 0·669–1·0 in B.Th.U. per gal.*	*Latent heat in B.Th.U. per lb. of oil of*	
		sp. gr. 0·8251	*sp. gr. 0·7796*
300° F.	700	102	108
350° F.	662·5	96	102
400° F.	625	91	96
450° F.	587·5	85	90
500° F.	550	80	85
550° F.	512·5	74	..
600° F.	475	69	..

(*l*) **Coefficient of Expansion.** The coefficients of expansion of volume of oil with increase in temperature are generally related to the specific gravity and to the actual temperature range. There is no doubt, however, that the chemical composition of the oil has a considerable effect on the coefficient of expansion. Little data has, however, been published on this subject. For the calculation of quantities of oil in bulk the figures given in U.S. Bureau of Standards Circular No. C410 are generally accepted.

(*m*) **Solubility of Water in Kerosine.** The solubility of water in kerosine is so small that its determination, owing to absorption from the air, presents extreme difficulties. Nevertheless the solubility/temperature curve is sufficiently steep to cause a distinct separation of water from kerosine packed in cans at a high temperature, when transported to a climate of lower temperature. This separation of water may effect corrosion of containers and therefore be of sufficient importance to merit consideration. E. Groschuff [14, 1911] gives the solubility of water in American water-white kerosine of specific gravity 0·794/0·796 and boiling-range 190 to 250° C. as shown in Table VIII. It appears probable that the solubility of water in a kerosine of aromatic type would be greater than that in one of paraffinic type.

Colour Stability

Consumers only too often demand qualities such as good odour, good colour, and colour stability, which are of little technical value, the attainment of which imposes on the refiner extra trouble and expense all to no purpose, other than to satisfy the demands of fashion and taste.

The causes of the deterioration of the colour of kerosine and the treatment necessary to avoid it have received much attention during the last few years. The results of this work have been published mainly in the *Proceedings of the World Petroleum Congress* of 1933. Colour instability is not a simple phenomenon as there are different types of such instability. Various means of detecting the tendency to discolour before actual discoloration takes place have been worked out, so that refining treatment can now be controlled so as to produce an oil which will retain its colour under reasonable storage conditions.

TABLE VIII

Temperature ° *C.*	*Solubility of water by weight* %
−2°	0·0012
18	0·005
23	0·007
30	0·008
36	0·012
53	0·026
59	0·031
61	0·035
66	0·043
79	0·063
85	0·075
94	0·097

Hillman [16, 1933] discriminates between the several types thus:

(1) A clear lemon-yellow type very erratic in its development, the most common in refined kerosines. It is an oxidation effect not apparently limited to any definite set of compounds, it develops in the dark and is almost entirely bleached by exposure to sunlight.

(2) A somewhat similar type which may or may not be light sensitive related to the presence of amino-bodies.

(3) A type due to the presence of cracked compounds. These are however generally absent from commercial kerosines.

(4) An unbleachable brownish discoloration which slowly develops only after very long periods of storage, and long exposure to light and which is, therefore, of relatively little importance.

He concluded from the fact that the discoloration of type (1) was bleached by various reducing agents that it was an oxidation product, and therefore tried to simulate it by various oxidation processes. He found that treatment with lead peroxide in dilute caustic soda produced a discoloration of the type required. Various samples which had gone off colour by long storage in the dark behaved on exposure to sunlight in precisely the same way as did the samples artificially oxidized to the same colour, the identity of behaviour being remarkable seeing that the natural colour was produced in 3 months and the artificial in 3 minutes.

McHatton [31, 1933] and Moerbeek [36, 1933] working on the same subject concluded that discoloration on storage was a result of the presence of certain so far unidentified phenols or hydroxyl compounds of hydrocarbons having properties resembling those of cyclopentadiene derivatives, and also in some cases of the presence of nitrogen bases. The presence of such bodies in very minute concentrations is sufficient to bring about strong discoloration. Thus Moerbeek found that the addition to a very good kerosine of carvacrol or nitrogen bases made from kerosine distillate, in the proportion of 1: 25,000 brought about a rapid deterioration in colour. A slight alkalinity also accelerated the discoloration to a surprising extent. This is of importance, as ships' tanks are often cleaned out with the help of caustic soda, a practice which in the light of the work of these authors should not be permitted where kerosine transport is concerned. Even traces of alkali on the inner surfaces of bottles used for storing samples may assist greatly in producing discoloration and so lead to false estimates of the quality of the kerosine in this respect. Bottles for retaining samples of kerosine should therefore be well cleaned with boiling water. These authors followed up their work by devising tests which might be applied to a refined kerosine in order to judge whether the degree of refining was sufficient to ensure the colour stability of the product on storage for periods of several months.

Hillman succeeded in working out a definite lead peroxide test which has proved of great practical value.

The test is carried out in the following way:

> Standard lead peroxide for this purpose is obtainable in capsules containing 1 g. This is dispersed in 20 ml. of 0·175 N. caustic soda solution. After thorough wetting of the lead peroxide with the caustic soda 700 ml. of kerosine at 30° C. are then added and the mixture thoroughly stirred for exactly 60 sec. It is then allowed to settle for 5 min., all these operations being carried out in the dark, and the colour then determined. The difference between the colours before and after treatment indicates the colour stability. As in general only water-white kerosines are tested, the colour after the treatment can be taken as the figure of the test.

Hillman points out that a negative test is not in itself a guarantee that kerosine so refined will be colour-stable, but he does assert that one which develops a colour in the carrying out of this test will certainly be very liable to go off colour on storage. Moerbeek [36, 1933] describes a test devised by Moser for detecting the presence of minute quantities of nitrogen bases by means of silico-tungstic acid.

The stage has not yet been reached where the refiner can predict with certainty that a kerosine will not go off colour on long storage, but a great advance in this direction has undoubtedly been made. It is obvious that this colour is produced by very small traces of strongly coloured bodies, the presence of which has no effect whatever on the burning qualities of the kerosine. The possibility of their formation, however, must be removed in order to satisfy the taste of the consuming public for a colourless oil. It has been found in practice that an insufficiently refined oil which will remain colour-stable in a storage tank at the refinery for months frequently discolours when subjected to pumping operations, &c. The close contact with metal, particularly copper, appears to catalyse the oxidation, resulting in the formation of coloured compounds. The discoloration of kerosine in tins also presents a serious problem, since the oil cannot without great expense be returned to the refinery for re-treatment. In this connexion J. B. Rather and L. C. Beard [43, 1936] describe the use of a number of oxidation inhibitors which will prevent the kerosine discolouring. These include hydroquinone, pyrogallol, resorcinol, phloroglucinol, thiocarbanilid, alkyl-substituted dihydroxy benzenes, ethanolamines, urea and thio-urea, &c., the stabilizer being used in the proportion of about 1 part by weight to 100,000 of kerosine. The polyhydroxy benzenes, such as hydroquinones, pyrogallol, &c., also possess the property of decolorizing kerosine which has gone off colour in storage. For this purpose 1 lb. of hydroquinone, for example, is dissolved in isopropyl alcohol or ethyl alcohol and added to 2,000/15,000 gallons of discoloured oil. Successful treatment of discoloured kerosine is also claimed with the use of oil-soluble blue-violet dyes.

If local retreatment of discoloured kerosine is necessary it is usually effected by filtering through one of the well-known types of decolorizing earth.

General Applications

Kerosine is used at present mainly as:

(*a*) An illuminant and heating agent.
(*b*) Motor fuel.
(*c*) A component of various industrial products.

(*a*) By far the largest quantity of kerosine is used as (1) a burning oil in lamps of either the wick-fed or vaporizing type, and (2) a heating agent in stoves, fires, and radiators, &c., which may be of either type. In the U.S.A. a light furnace oil, which is substantially a heavy unrefined kerosine is used largely for central heating purposes. The potential market for kerosine in these directions is great, particularly in the more undeveloped countries where alternative lighting systems are not available. Improvements both in the design of lamps and stoves and in the refining of kerosine will lead to more general recognition of the merits of this long-established commodity.

(*b*) In countries where agriculture and fishing industries are of importance, kerosine is used as a fuel in engines of the spark-ignition type fitted to tractors and fishing boats. Engines of the hot-bulb type also employ kerosine, but such engines are becoming less popular owing to the increasing efficiency and availability of those of the compression-ignition type.

(*c*) More extensive use of kerosine is being made in the manufacture of bituminous products for road construction, insecticides, anti-malarial oils, agricultural preparations, such as cattle and sheep dips, polishes, paints, and so forth. It is also used for degreasing and cleaning processes, for washing coal by froth flotation and for the extraction of naphthalene from coal gas.

Of these the most important application of kerosine is in the manufacture of cut-back asphaltic bitumens for the treatment of roads. These are discussed in the chapter on asphaltic bitumens (p. 2690), but from the kerosine point of view it is sufficient to indicate that with cut-backs used for surfacing roads the kerosine is generally as volatile as possible (subject to Customs or other requirements) in order to facilitate evaporation of the kerosine from the cut-back material after application to the road.

Most domestic insecticides contain a proportion of kerosine, the main characteristic of which is freedom from odour, which is obtained by heavy chemical treatment or solvent extraction to remove the aromatic hydrocarbons, &c. The kerosine should have a high flash-point, in order to reduce the risk of fire, and a low final boiling-point in order that it should evaporate readily.

Although kerosines find many other industrial applications in connexion with the manufacture of paints, polishes, cleaning, and degreasing compounds, &c., the quantities used are small, so that generalizations as to the properties of kerosines for such diverse applications can obviously not be put forward, apart from the more obvious features, i.e. the desirability of a high aromatic content and a high volatility where solvent power and rate of evaporation are of importance.

It will be obvious that, as kerosine is used for such different purposes, the quality of a kerosine can only be estimated in relation to the purpose for which it is used.

Fortunately the refiner is able to modify the physical properties, such as volatility and viscosity, by controlling the conditions of distillation, and the chemical composition by the use of solvent extraction processes, so that kerosines of highly aromatic or highly paraffinic nature may be produced to meet the most diverse requirements. Naturally the type of crude oil available to the refiner places some restriction on his capability to produce any required type.

Kerosine for Lighting and Heating

The lamps and stoves in which kerosine is burnt fall into three main categories: (*a*) wick-fed white flame, (*b*) wick-fed blue flame, and (*c*) vaporizing.

(*a*) Wick-fed White Flame Appliances.

Wick-fed lamps have been produced in a bewildering variety, ranging from the home-made lamps of the East, often constructed from the simplest materials such as metal polish tins, ink bottles with a wick of string or vegetable pith, or even a piece of rag, to the lighthouse burner with nine concentric circular wicks, which has now become extinct. The many types of household lamps in general use display fundamental differences in design, such as in depth of reservoir, type of wick, and particularly supply of air to the wick, and type of chimney. Of such diversity are these types that a particular kerosine which burns well in one lamp may burn badly in another, while two kerosines may be rated in quite different manners by two different lamps. The properties of kerosines should therefore be considered in relation to the types of lamps in which they are to be used.

The three fundamental requirements of a good kerosine for use in wick-fed lamps producing a self-luminous flame, are:

1. It must give a flame of good initial candle-power.
2. It must maintain this candle-power as the oil burns.
3. It must not give rise to excessive deposits of film on the chimney.

1. **Initial Candle-Power.** The size and brilliancy of the flame depends on the chemical composition of the kerosine in relation to the design of the lamp. The chemical nature of a kerosine reflects that of the crude from which it is distilled. Although the quality of kerosines has on the whole been much improved in the last decade or so (mainly by the use of the Edeleanu process), there is still great diversity of character displayed by the kerosines on the market at the present time (*vide* Table II, p. 2471), as the demands for oil and the types of lamps show great diversity dependent largely on the wealth of the purchasers. In the Far East, for example, lamps of a very primitive type, little better than those of ancient Rome or Greece, are stil in use. In such types of lamp the best oils burn badly and the worst nearly as well as the best. In such areas, therefore, kerosines of inferior burning quality which will only give small flames and will therefore last a long time are marketed.

The three types of hydrocarbons show great differences in behaviour in any given type of lamp. In general, it may be stated that in lamps with a poor draught kerosines composed mainly of paraffins burn well, while those rich in naphthenes, and especially aromatics, burn with a reddish and even smoky flame. In a suitably designed lamp with a good draught, the most aromatic type of kerosine will burn brilliantly and well, whereas in the same lamp the paraffin type may burn with a flame of weak luminosity.

This renders attempts to compare the amount of illumination given by flames from different types of kerosine in similar lamps under similar conditions rather misleading, as the total illumination from a flame is a product of the size of the flame and the intrinsic brilliancy, which factors are affected both by the design of the lamp and by the chemical composition of the kerosine.

Effect of Lamp Design. The effect, in particular, of the draught in a lamp on the size of flame produced, has been studied by Minchin [33, 1933], who used a special lamp with a flat wick burner, in which the draught could be varied by using a taller chimney or by adjusting the position of the flame deflector. He showed that by increasing the draught the fuel consumption and the size of the flame was reduced. The reduction in the size of the flame was, however, greater than that expected from the reduced fuel consumption, so that the effect of increased draught is also to compress the volume of gas within the luminous envelope. The increased draught increases the pressure over the wick and thereby decreases the rate of evaporation, but at the same time requires a greater pressure in the gas within the luminous envelope in order to balance the overhead pressure.

It is also shown that under conditions of increased draught, the brilliancy of the flame increases, to a certain maximum. The luminosity of the flame being due to the cloud of carbon particles formed by the cracking of the kerosine, any factors which affect this concentration of carbon particles will affect the luminosity of the flame. The size, concentration, and type of the carbon particles are controlled by the conditions under which the kerosine is cracked, so that relatively slight variations in these conditions may have quite an appreciable effect on the luminosity. Thus, the method of introduction of air (i.e. internal or external draught, and location of air holes), the type and height of chimney and type of burner, amount of wick extended, &c., affect the temperature or pressure conditions during cracking and thus play a large part in determining both the size and luminosity of the flame.

Effect of Chemical Composition of Kerosine. The increase in luminosity by increasing the concentration of the cloud of carbon particles in the flame may also be obtained by using a fuel with a higher carbon content, e.g. an aromatic type kerosine. At the same time a very much smaller and reddish flame is given with this type of kerosine. Minchin [33, 1933] illustrates the effect on the candle-power of the addition of tetralin to a paraffinic type kerosine in a Saybolt lamp with a flat flame (*vide* Table IX).

The question as to whether the addition of aromatic hydrocarbons to a kerosine increased or decreased the total candle-power of the flame has been discussed between W. Danaila, V. Stoenescu, and S. Dinescu [10, 1930; 11, 1932; 12, 1933], on the one hand, and W. Grote and E. Hundsdörfer [15, 1932] on the other.

The former found that up to a certain limit (depending on the type of kerosine), the addition of individual aromatic hydrocarbons or Edeleanu extracts of kerosine increased the total candle-power of the flame in a small Luchaire lamp (Roumanian Railways model). The latter investigators, however, were unable to confirm these results, either in a Luchaire (flat wick) lamp or a lamp fitted with a Cosmos burner (circular wick).

Whether an aromatic or a paraffinic type kerosine will give more light when burnt in the same lamp will depend, largely, on the design of the lamp. The relation of the flame height to the chemical composition of the kerosine is discussed fully later, but it is sufficient at this stage to indicate that under ordinary conditions, paraffin hydrocarbons give the greatest flame height, naphthene hydrocarbons a much smaller height, and aromatic hydrocarbons the smallest. In a normal flat-wick lamp with moderate draught, the increased size of flame given by a paraffinic type of kerosine will generally outweigh the greater intensity of the smaller flame given by an aromatic type kerosine. In circular wick lamps, particularly those with good draughts, the flame of a paraffinic type kerosine may be so reduced that the total candle power may be less than that of the aromatic type kerosine with a more intense flame.

TABLE IX

Fuel	*Sp. gr.*	*Candle-power*	*C.P. per sq. cm. of flame*
Paraffinic:			
Aromatic free . . .	0·768	16·0	0·588
Pennsylvanian (P) . .	0·777	14·2	0·591
97·5% P. + 2·5% Tetralin .	0·781	15·2	0·630
95·0% P. + 5·0% ,, .	0·786	14·7	0·641
92·5% P. + 7·5% ,, .	0·793	14·1	0·650
85·0% P. + 15% ,, .	0·808	13·6	0·680
80·0% P. + 20% ,, .	0·818	12·4	0·720
70·0% P. + 30% ,, .	0·841	10·3	0·766
60·0% P. + 40% ,, .	0·858	5·2	0·766
100% ,, .	0·950	..	0·950 (extrapolated)

The differences in the candle-power of kerosines burnt in different lamps is further emphasized by the results of a series of tests of four kerosines in four different lamps [41]. Four lamps were chosen as representing different types in common usage:

1. Double flat wick (external draught).
2. Circular wick type with deflector (central draught-air supply taken through vertical channel in reservoir).
3. Single flat-wick type (external draught).
4. Split circular wick type with deflector (central draught-air supply taken through side of burner).

Four kerosines of different chemical composition (taken from those in Table II, p. 2471) have been burnt in these lamps and the initial candle-powers determined under two sets of conditions:

(*a*) kerosines burnt at their maximum flame height without smoking in each lamp.

(*b*) kerosines burnt at the same rate of consumption in each lamp.

(*a*) *At Maximum Flame Height.*

TABLE X

	Kerosine			
	No. 21	*No. 18*	*No. 7*	*No. 1*
Aromatic content . .	40%	22%	11%	3%
Smoke-point . . .	12	21	25	41
Initial candle-power in:				
Lamp 1	*	33·5	32·7	42·8
Lamp 2	23·1	28·0	27·5	31·0
Lamp 3	*	18·8	18·5	23·8
Lamp 4	6·0	18·5	18·5	24·0

* Could not be burnt.

(b) At Same Consumption.

TABLE XI

	Kerosine				*Rate of consumption g. per hr.*
	No. 21	*No. 18*	*No. 7*	*No. 1*	
Aromatic content .	40%	22%	11%	3%	..
Smoke-point . .	12	21	25	41	..
Initial candle-power in:					
Lamp 1 . .	*	24·5	23·2	24·1	53
Lamp 2 . .	23·1	23·0	23·2	22·4	53
Lamp 3 . .	*	14·3	12·9	13·9	36
Lamp 4 . .	6·0	7·0	6·3	6·9	27

* Could not be burnt.

The figures in Table X indicate that: (1) in ordinary flat-wick type lamps with not very good draughts (types 1 and 3) highly aromatic kerosines cannot be burnt, but in lamps of special type with a good draught (type 2) they can be burnt quite successfully, but give smaller flames and lower candle-powers than the paraffinic type kerosines. In type 4 lamp, however, possibly owing to weaker draught, the highly aromatic kerosine gives only a very small flame. The highly paraffinic type kerosine gives the greatest candle-power in each lamp, probably owing to the much larger flame obtainable (compare the smoke-points of each type).

With regard to kerosines of types 18 and 7, it will be seen that the more aromatic kerosine gives a slightly greater candle-power (or identical in type 4 lamp) than the less aromatic type. This may be attributed to the more intense flame given by type 18 with 22% of aromatics, as compared with type 7 with only 11% of aromatics, being only partially offset by the greater flame obtainable with type 7 (smoke-point 25 as compared with 21 for type 18).

The effect of the greater flame height given by the paraffinic type kerosines is largely removed in the tests described in Table XI in which the kerosines were burnt at the same rate of consumption. Here again the highly aromatic type kerosine could not be burnt in the flat-wick type lamps, but in the circular-wick types it gave practically the same candle-power as the paraffinic type kerosines. If, therefore, the rate of consumption is restricted to that at which the most aromatic type will burn, all the kerosines burn giving practically the same candle-powers. This does not necessarily suggest that flames of the same size from aromatic and paraffin type kerosines give the same candle-power, but that the same amount of kerosines of different types burnt in the same lamp gives the same candle-power. It appears probable that as in the case of the results given in Table XI, the aromatic kerosines give smaller but more intense flames per unit weight of kerosine burnt than the paraffinic type kerosine. The conditions in these tests are such that these two factors cancel each other.

It is apparent from the above figures that owing to the great variation in type of lamp, candle-power determinations will not indicate whether a certain kerosine will give a satisfactory light in all types of lamps. Also, there is considerable difficulty in trimming lamp wicks so that two identical kerosines in two identical lamps give the same flame height.

In general, it may be stated that there are two main types of lamps in general use, one with a flat wick which prefers a paraffinic type kerosine, and the other, generally smaller with circular wick and central draught, which is not so particular in its requirements. More attention has therefore been paid to satisfying the requirements of the flat-wick type lamp, e.g. by the introduction of the Edeleanu process. In this type the candle-power given depends largely on the height of flame obtainable, this varying with the chemical composition of the kerosine. It therefore becomes desirable to devise some standard apparatus for comparing the height of flames given by different kerosines which could be related to the size of flame given in flat-wick lamps.

Smoke-point Test. The problem was attacked by the Laboratory of the Bataafsche Petroleum Maatschappij in 1926 and a lamp evolved in which could be determined the maximum height in millimetres at which a small kerosine flame would burn without smoking. As 32 mm. was the maximum height for the best kerosine then on the market, the tendency to smoke was taken as 32 minus the actual flame height of the kerosine in question.

The apparatus suggested by them has now been modified and standardized by the Institution of Petroleum Technologists, the actual maximum flame height being reported as the Smoke-point (in view of the fact that kerosines with smoke-points over 32 are now on the market) (Fig. 1).

The apparatus used consists of a specially constructed lamp in appearance like an old-fashioned carriage candle lamp. This is fitted with a small kerosine container fitted with wick tube and a device for raising or lowering the flame. Behind the flame is situated a scale, graduated in millimetres, the zero mark being level with the top of the wick guide. The height of the flame is observed against this scale through the concave glass door.

In order to carry out the test 10 mm. of the kerosine are introduced into the clean, dry container. A piece of standard wick not less than 5 in. in length previously extracted with a suitable volatile solvent and dried for half an hour at 100° C. and after soaking in the sample under test is fixed in the wick holder and this in the lamp. The wick should project 3 mm. above the end of the wick holder. After the lamp has been burning for 5 min., the oil being kept at from 20 to 25° C. and the flame about 10 mm. high, the test is made by raising the wick until the flame smokes slightly, then reducing the height carefully until the smoky tail just disappears. The height of the flame at this point gives the value of the smoke-point test directly on the scale. For full details as to the standardizing and use of the apparatus the Institution of Petroleum Technologists Standard Method Book should be consulted [47, 1935].

With the help of this apparatus Kewley and Jackson [24, 1927] and later Minchin [32, 1931] explored the effect of chemical composition on the initial candle-power. Minchin used specially prepared kerosines of various types approximating as far as possible to paraffins, naphthenes, and aromatics. A kerosine of the paraffinous class was prepared by the method of Minchin and Nixon [34, 1928]. Paraffin wax when cracked at relatively low temperatures yields a distillate composed mainly of saturated paraffins and unsaturateds. As aromatics are formed only under high-temperature conditions, the absence of naphthenes would be expected. This was confirmed by the work of Sachanen and Telicheyev [46, 1927] on the cracking of paraffin wax. Minchin used the fractions made by distillation through a Hempel column between 150 and 280° C. That made from the cracking of wax was considered as the paraffin type. The naphthene type was made from Badarpur (Assam) crude by removing aromatics by sulphonation and was found by Carpenter to be practically purely naphthenic in composition [9, 1926]. The aromatic type was prepared by Nixon's method of repeatedly cracking an aromatic extract at temperature of 400/500° C.

The kerosines so obtained had the properties:

TABLE XII

	Sp. gr. at 60° F.	Aniline point
Paraffin type	0·763	82·8° C.
Naphthene type	0·841	54·0° C.
Aromatic type	0·925	below 0° C.

By studying the behaviour of kerosines made of various admixtures of these types, Minchin [32, 1931] arrived at the conclusion that the tendency to smoke was directly proportional to the aromatic and naphthene content.

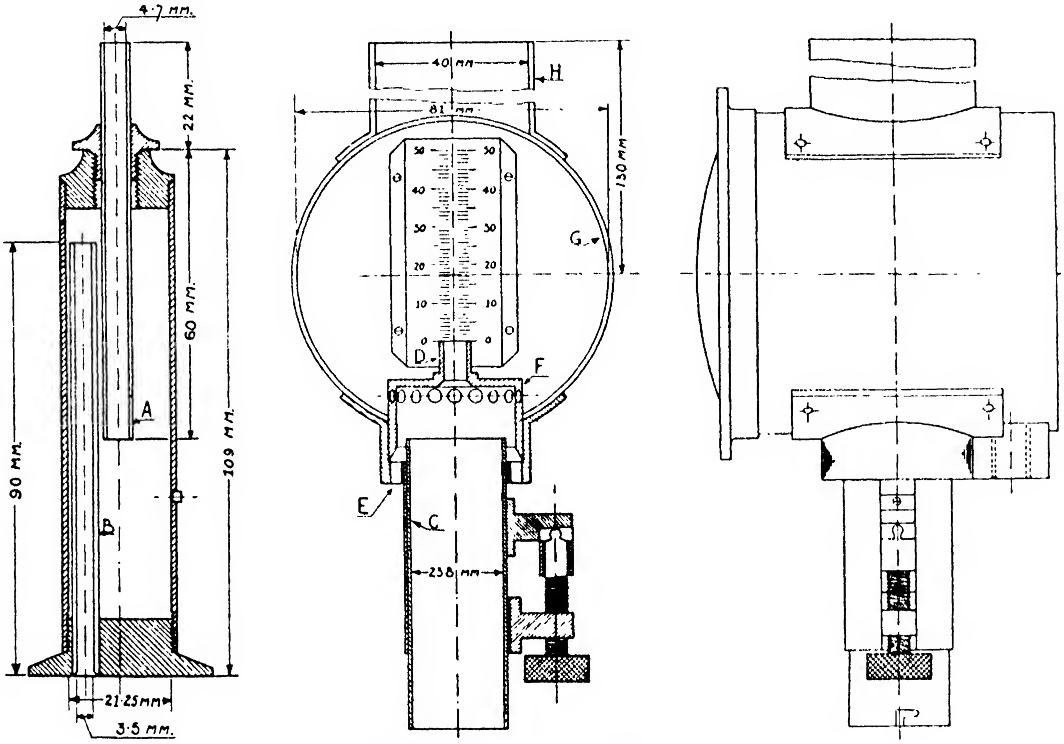


FIG. 1. I.P.T. smoke-point lamp.

Kewley and Jackson [24, 1927] similarly, using two components—one a heavily treated paraffin type kerosine and the other a liquid sulphur dioxide extract from a highly aromatic natural kerosine—found the following figures:

TABLE XIII

Paraffin component %	*Aromatic component* %	*Smoke-point*
100	0	32
95	5	29
90	10	26
85	15	22
80	20	20
70	30	14
60	40	10

The smoke-point of a kerosine rich in aromatics was changed from 15 to 30 by the removal of the aromatics by sulphonation. An indication of the relative value of paraffins and naphthenes was obtained by comparing two kerosines of the same boiling-point range, one from a light Mexican paraffinous crude and one from a Sarawak crude, both heavily sulphonated to remove aromatics.

TABLE XIV

	Sulphonated Sarawak	*Sulphonated Mexican*
Specific gravity at 15° C. .	0·838	0·774
Boiling range . . .	170–270° C.	170–270° C.
Smoke-point . . .	20	32

Minchin (loc. cit.) further concluded that there was a decrease in smoke-point with increase in molecular complexity. He also explored the smoke-point of homologous series of hydrocarbons and found except in the case of the paraffin series, the smoke-point increases with the number of carbon atoms in the molecule, a statement which at first sight seems to conflict with that made in the previous sentence. It is doubtless to be explained by the fact that the higher hydrocarbons of the benzene or naphthene ring type, actually present in kerosine, contain side chains of a paraffin nature. As their complexity increases they tend to behave more like paraffin hydrocarbons, i.e. their smoke-point decreases with boiling range. Thus the effect of the true higher benzene and naphthene ring hydrocarbons in raising the smoke-point is more than offset by the combined effect of the higher paraffin and of the complex benzene or naphthene ring hydrocarbons with side chains in lowering the smoke-point. Minchin gives the example shown in Table XV. From the above it will appear that the smoke-point test really renders unnecessary such tests as aniline point and percentage extractable by sulphuric acid. It supplies all the information necessary as to the relative amounts of paraffins, naphthenes, and aromatics from the point of view of practical illuminating value.

In addition to giving an indication of the maximum size of flame at which the kerosine can be burnt without smoking, and thus the initial candle-power, the smoke-point test gives an indication of the ability of the kerosine to burn in a draughty situation without smoking. As a sudden draught will extend the flame of a kerosine, the higher the smoke-point the less tendency there will be for the flame to reach its maximum height and to commence smoking. A further feature in connexion with the smoke-point test is that, as a larger flame is obtained with a kerosine of high smoke-point, a larger consumption of kerosine must be expected. This is frequently of importance from the marketing point of view and accounts for the larger sale of inferior kerosines of low smoke-point—those giving low rates of consumption—in native areas.

TABLE XV

Fraction range, ° C.	*Smoke-point*
140–150	24·7
150–160	23·5
160–170	22·8
170–180	22·6
180–190	22·1
190–200	21·1
200–210	20·1
210–220	19·3
220–230	18·3
230–240	17·8
240–250	17·1
250–260	16·3
260–270	15·3
270–280	14·3

A similar test is described by J. B. Terry and E. Field [52, 1936] who have modified the original Davis Factor Lamp designed in 1923. The kerosine is burnt in a small lamp with a reservoir of capacity 4 oz. and fitted with a glass chimney 1 in. in outside diameter and 7 in. long. The lamp is burnt for 15 minutes, using a small flame and the wick then turned up until the smoking starts, the actual point being detected by the formation of a smoke spot on the underside of a porcelain dish filled with cracked ice and held over the chimney. The dish is then removed and the flame turned down one-half of a division on the scale behind the flame (0·05 in.), this being repeated until the maximum height of flame is produced without a smoke-point forming on the dish. The smoke-tendency factor is then read off on the scale. Very highly refined kerosines give flame heights of 3·00 in. or more, well-refined grades about 2·00 in., and inferior grades less than 1·00 in. Results are reproducible to within 0·05 in. flame height for most kerosines, and to within 0·1 in. for very highly refined grades.

(2) **Maintenance of Candle-power.** The second qualification, the maintenance of the candle-power as the kerosine is consumed, has, up to the present, not been so fully investigated. It depends on (A) a constant supply of kerosine to the wick and (B) complete combustion of the kerosine without char formation on the wick.

(A) *Constant Supply of Kerosine to the Wick.* The supply of kerosine to the wick depends on its viscosity at the oil temperature and on the design of the lamp, in particular the 'lift', i.e. the distance between the top of the wick and the oil-level.

Design of Lamp. No kerosine can maintain its burning qualities in a lamp with a deep, narrow container, such that as the oil is consumed the distance between the level of the surface of the oil and the top of the wick increases greatly. The following figures show the candle-powers given by two identical burners with the same kerosine, the only difference being in the containers, one of which was of such large diameter that the height of the wick top above the level of the oil dropped not more than an inch during the test, while the other was of such narrow diameter that the drop of level amounted to 9 in.

TABLE XVI

Time	*Candle-power*	
	Shallow reservoir	*Deep reservoir*
0 .	20·0	20·0
1 hour .	20·6	13·8
4 hours .	21·8	12·0
8 „ .	21·8	11·0
12 „ .	21·8	10·2
15 „ .	oil consumed	2·6

The behaviour of the kerosine in the shallow reservoir lamp indicates that no change in the composition of the kerosine takes place during the burning. It would hardly seem possible that any such effect would show up, but the point was settled by Nakamura as long ago as 1883 [38].

Viscosity. Kewley and Jackson [24, 1927] determined the viscosity of a number of typical kerosines of approximately the same boiling-point range and found considerable differences not only in the actual viscosities, but also in the viscosity/temperature curves.

Fig. 2 shows several such curves, from which it will be noticed that the three lower curves (paraffinous type) are less steep than the three upper (naphthenic type):

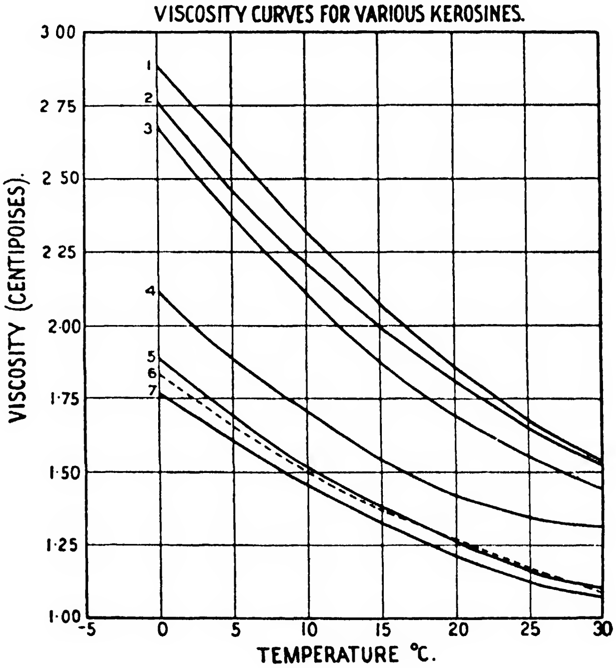


FIG. 2.

The viscosities were determined by the No. 1 Ostwald type of viscometer [7].

If the viscosity is not sufficient to ensure an ample supply of kerosine to the wick, as the level in the reservoir falls the flame decreases. If a decrease of flame height be corrected by turning up the wick, the rise in candle-power is only temporary. As soon as the surplus kerosine so obtained burns off, the then over-protruding wick carbonizes, adding a further trouble to that of the decreasing illuminating power. A kerosine which burns with a large flame in a particular lamp would require a lower viscosity than one which burns with a small flame. As the viscosity increases with increase of boiling-point, it must be adjusted not only to the chemical composition of the kerosine, but also to its boiling-point range, and also to the temperature of the atmosphere in which the kerosine burns.

The influence of the depth of the container is now obvious. For kerosine testing, therefore, a very shallow reservoir of large diameter should therefore always be used.

In general the viscosity of a kerosine should not exceed 2·0 centipoises at the temperature at which it is to be used [21, 1933].

Capillarity. The rate at which the kerosine is fed to the wick depends not only on the viscosity, but to a less extent on the capillarity of the kerosine. Stepanoff [49, 1906] developed the following formula for the amount of kerosine drawn through a wick:

$$M = \frac{\alpha^2}{Z},$$

where M = quantity drawn through the wick,
α = capillarity constant of kerosine,
Z = viscosity of kerosine.

The capillarity constant is a complicated factor which can generally be regarded as a constant for most normal kerosines for a given wick under fixed conditions, since its variation is much less than that of the viscosity. Holde [19, 1933] gives a figure of 2·7/2·8 mg./mm. for the capillarity constant of kerosine. Engler and Levin [13, 1886] found little difference in the capillarity of different fractions from (*a*) Caucasian and (*b*) American kerosines. They conclude that the rate of supply of kerosine to the wick is a function of the viscosity and of the specific gravity.

Fig. 3 illustrates the variation of capillarity (measured by the height attained by the kerosine up a capillary tube) with temperature, the kerosines tested being some of those shown in Fig. 2. In general, kerosines with high viscosities have high capillarities, although the individual differences in capillarity values is quite small. The capillarity decreases with rise in temperature, but to a much smaller extent than does the viscosity.

It therefore appears probable that a high viscosity in a kerosine will be slightly offset by the high capillarity, but there is no doubt that the viscosity is the more important factor.

Kerosines of high viscosity are frequently marketed in tropical countries, and in view of the difficulty of burning such oils in standard lamps at ordinary temperatures, they should be tested in a room the air of which is heated to that at which the oils will be burnt by the customers. Similarly, oils marketed in very cold countries should be examined in a cold room, as the increase in viscosity may make a considerable difference to the burning of the oil. Also, the lower temperature of the lamp glass may be more conducive to excessive bloom deposition.

Lamps have been designed to burn heavy kerosine, by modifying the burner so that it dips into the oil, thereby raising its temperature and lowering its viscosity.

In ordinary lamps, the greater lift of the kerosine as the level falls is generally slightly offset by the increased viscosity of the kerosine caused by the warming up of the containers by conduction from the burner. In this connexion a glass reservoir would remain cooler than a brass reservoir. The actual difference in temperature, of course, varies with the type of lamp, but with lamps of the A.S.T.M. Saybolt type the difference in temperature between the oil in the container and that of the atmosphere does not generally exceed 5° C.

(B) *Char Formation on Wick.* The second characteristic relates to the formation of a carbonaceous incrustation or 'char' on the wick of a lamp after it has been burning for some time. This char which may be hard and brittle or soft and powdery is easily detachable from the wick and is evidently formed from the kerosine itself. It may occur in irregular localized deposits 'mushrooms' which produce distortion of the flame and lead to smoking, or as a general deposit which encloses the surface of the wick and restricts the size of the flame, eventually leading to its extinction. The cumulative effect of char formation is frequently reduced by the falling off of large particles of char if the lamp is moved, so that this factor must be taken into account when carrying out burning tests for an extended period of time.

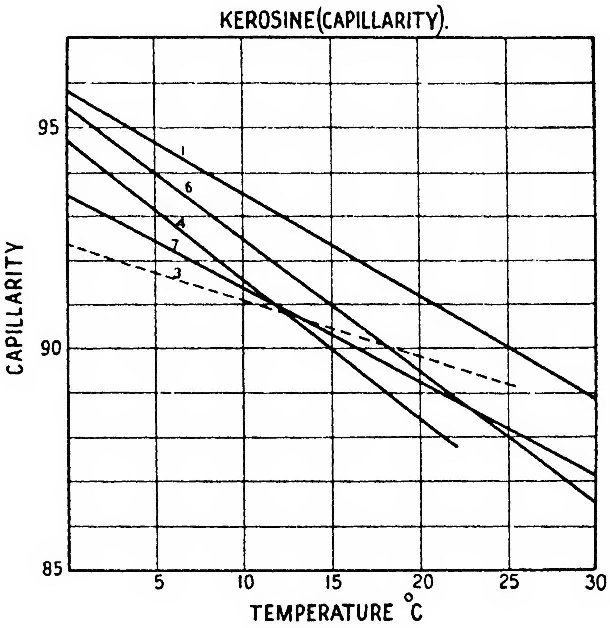


FIG. 3.

As a method of determining char formation Jackson [21, 1933] recommends the use of the A.S.T.M. Saybolt lamp (D. 187–30) modified by the addition of a constant-level device adjusted so that the 'lift', i.e. the distance between the top of the wick and the surface of the kerosine, is 80 mm. After burning for 24 hours the char is very carefully detached from the wick and weighed. The following results of tests on four different commercial kerosines illustrate the wide variation in the amount of char formed by normal kerosines on the market.

TABLE XVII

	Weight of dry char per litre of oil burnt
Kerosine A	66
„ B	56, 59 (2 tests)
„ C	18
„ D	8

The Institution of Petroleum Technologists has tentatively standardized a burning test [48, 1935] in a simpler type of lamp, not fitted with a constant-level device. For most kerosines of fairly low viscosity the two lamps do not give very different results, but the constant-level device facilitates the burning of kerosines of fairly high viscosity. In tests, therefore, where the char value due solely to the chemical characteristics of the kerosines is required, the former test is more suitable. Where, however, the char value, possibly affected by the viscosity of the kerosine, is required, the latter test may be regarded as more in line with practical conditions. However, in actual practice there is such a wide variation in the shape of the oil container, frequency of filling, &c., that it may be preferable to gauge the burning value of the kerosine under ideal supply conditions, and to make allowance for any viscosity effect, i.e. starving of the feed when the level of the kerosine falls.

Causes of Char Formation. As in the case of the candle-power of a kerosine flame, the char formation is affected by two considerations, (*a*) the design of the burner, and (*b*) the characteristics of the kerosine.

(*a*) A consideration of the fact that the same kerosine when burnt in lamps with different burners gives different char values renders it obvious that the design of the burner is responsible for at least a portion of the char formation. The amount and type of char formation is probably related to the way in which the kerosine breaks down in contact with the wick. Temperature and pressure conditions resulting from the method of introduction of the air, &c., undoubtedly play a part determining whether the decomposition produces, in addition to carbon particles, any heavy residues difficult to burn under the conditions obtaining at the wick. An investigation of the cracking characteristics of different kerosines might throw some light on this problem. There is no doubt that char formation when burning any type of kerosine could be considerably reduced by adjustment of the design of the lamp, but so far this has received very little attention. The char formation is accelerated by undue cooling of the wick, as when it is turned up high in order to obtain a greater supply of oil to the flame. Wicks with a high ash content also have been found to give higher char values than those with low ash contents.

(*b*) With regard to the effect of the characteristics of the kerosine on the char formation, Jackson [21, 1933] considers the presence of the following important:

(1) Unsaturated bodies.
(2) Sulphur compounds.
(3) Aromatic hydrocarbons.
(4) Fractions of relatively high boiling-point.
(5) By-products of refining.
(6) Dye or other contaminating bodies.

(1) Moerbeek [36, 1933] states that kerosines containing unsaturated hydrocarbons produced by cracking give heavy char formation, but such kerosines are not used to any extent in wick-fed lamps.

(2) Little information is available as to the effect of sulphur compounds on char formation. Moerbeek (loc. cit.) considers the sulphur content as such to have no effect on the incrustation. There is possibly, however, an indirect effect in so far as it is very difficult to refine a kerosine distillate of high sulphur content so as to produce an oil of low char value.

(3) Moerbeek (loc. cit.) considers kerosines with an excessive tendency to smoke liable to give heavy incrustation which, however, is softer and more amorphous and also less objectionable than that caused by other factors. It is certainly the case that edeleanized kerosines in general give less char formation than unedeleanized grades of the same origin.

(4) Moerbeek (loc. cit.) points out that while fractions of high-boiling range tend to give greater incrustation than those of lower boiling range, the effect is not so pronounced with edeleanized kerosines, so that with such grades higher final boiling-points are permissible than with non-edeleanized kerosines.

(5) He also confirms that the presence of by-products of the refining process, not removable by washing with soda, which have been formed by over-treating highly sulphurous distillates at too high temperatures will produce char. Thus a distillate refined to 0·1% of sulphur keeping the refining temperature down to 10–15° C. gave little char, while the same distillate refined to the same sulphur content but at a temperature of 30–35° C. gave a very heavy incrustation. A dark residue left when carrying out the A.S.T.M. distillation test usually indicates that the kerosine contains unstable fractions which will give rise to heavy char formation on burning.

The presence of appreciable quantities of sulphonic or naphthenic acids, or salts of these acids, may be detected by the 'Natron' test [20, 1935]. In this test the kerosine is extracted with caustic soda solution, the extract neutralized with hydrochloric acid, and the presence of soaps detected from the resulting turbidity of the solution. A layer of the solution in a test-tube of diameter 25 mm. should be sufficiently translucent to allow small type to be read through it. The 'Flock' test [8, 1927] also gives an indication of the presence of any impurities in the kerosine which are unstable to heat and therefore liable to give high char formation.

(6) The presence of contaminants such as fuel or lubricating oils are liable to cause high char formation, even when present in small quantities. In this connexion a char value of, say, 16 mg. per litre (I.P.T. lamp) corresponds to only 0·002%, so that the effect of a small quantity of contaminant may be very pronounced.

A special application of kerosine demanding the maintenance of good illuminating value over a long period is its use in railway signalling lamps. The kerosine is expected to maintain a steady flame of specified dimensions for 7 days without smoking. The suitability of a kerosine in this respect may be determined by the A.S.T.M. method (Serial Designation D. 219–30) or the I.P.T. method (Serial Designation L.T.B.O. 35). Baker [3, 1932] points out the necessity for high luminosity of that portion of the flame which is at the focus of the lens of the signal lamp.

The char value is also of the greatest importance in kerosine used in lamps in incubators, brooders, &c., where the lamps are required to burn for a long time with the minimum of attention. In the case of incubators and brooders a constant-flame size is of great importance. The formation of heavy char will reduce the size of the flame, and eventual extinction may endanger the safety of the eggs or chickens. On the other hand, the viscosity of the kerosine should not be too low, as the container tends to become hot owing to the lamp being burnt in an enclosed space. For this reason the flash-point of the oil should also be as high as possible. In the case of brooder lamps it is of importance that the oil should not evolve fumes, particularly of a sulphurous nature.

Wick-fed kerosine lamps were at one time largely used for lighthouse work, though they have now been superseded by the incandescent mantle vaporizing type (q.v.). In 1882 a Douglas burner having six concentric circular wicks giving a candle-power of 4,800 was installed in the Eddystone lighthouse and was later replaced by a 10-wick burner of 7,900 candle-power. The cooling of the wicks of such a burner was a difficult matter.

(3) **Formation of Film on the Chimney.** The third main qualification is that the kerosine in the course of burning should not give rise to heavy deposits of film on the lamp chimney.

The formation of such deposits depends not only on the hydrocarbon composition of the kerosine, but on its impurities, mainly sulphur compounds.

A brownish deposit indicates incomplete combustion with the production of smoke, and may be due to the formation of excessive char or to burning the kerosine in a draughty place. In the latter case a kerosine of higher smoke-point should be used.

A bloom of white, grey, or blue colour is due primarily to the effect of the sulphur content. Moreover, the formation of this bloom depends on two other factors, the temperature of the lamp chimney and the draught, and the purity of the atmosphere in which the lamp is used.

This question was investigated by Kewley and Jackson [24, 1927], who showed that the composition of the bloom depended on various conditions. It may contain sodium sulphate, ammonium sulphate, and organic acidic bodies from the oxidation of the sulphur compounds in the kerosine.

Alkali derived from the lamp chimney itself plays a part. It is found that, other things being equal, new lamp glasses give more bloom formation than do those which have been used and cleaned several times. The presence of ammonia in the atmosphere strongly accentuates bloom formation, as does the presence of fog, particularly of the smoky variety. The necessity of carrying out burning tests in a pure atmosphere is therefore obvious. However, even with used lamp glasses frequently cleaned and in a pure atmosphere bloom still forms on the chimneys of certain types of lamp with oils of relatively high sulphur content. The bloom so formed on a silica lamp chimney was found to consist of organic sulpho acids or bodies of a similar nature, and also sulphates of sodium with traces of potassium and calcium, probably derived from the wick.

The formation of bloom depends in any case largely on the design of the lamp chimney. The bulging type which keeps relatively cool is particularly prone to this trouble, whereas the long, narrow type, which is relatively much hotter, rarely shows a bloom formation even with a bad kerosine. A chimney which widens suddenly near the top (crimp top type) gives a less steady and powerful draught than a chimney which has straight sides or narrows evenly from the bulge. In the latter type of chimney a flame is therefore less liable to flicker. The whole problem of efficient burning of kerosine in wick-fed lamps is, however, intimately connected with the design of the lamp in which it is to be used; therefore to get maximum efficiency the lamp most suitable for the type of kerosine in question should be used.

(*b*) Wick-fed Blue Flame Appliances.

Blue flame burners are usually designed in such a manner that the flame burns in the annular space between two concentric cylinders both perforated with numerous holes. The design, dimensions, and arrangement of these holes are so correlated with the factors determining the draught that a blue hot flame is obtainable. Such burners give complete combustion so that if kept clean smell is practically absent. Many such stoves or cookers are fitted with a constant-level feed so that the falling off of the flame with fall of level in the reservoir is avoided. Certain cookers of this class are fitted with short asbestos wicks dipping into an annular reservoir supplied from the constant feed, arrangements being made for regulating the height of the flame.

Although the choice of kerosine as an illuminant is determined mainly by reasons of convenience rather than of economy, the cost of illuminating being small, in the case of heaters and cookers with relatively large oil consumptions economic considerations play a great part, the efficiency as well as the cost of the fuel coming into consideration.

There are few indications available to assist in the selection of a suitable kerosine for use in blue flame burners, but it is probable that the design of the burner is of not less importance than in the case of a white flame burner. In addition to possessing a low tendency to develop char under the particular conditions, it is important that the kerosine should not evolve vapours of an unpleasant odour or give products of combustion which attack the bottoms of cooking vessels. The sulphur content should therefore be as low as possible, but this is not always a guarantee that metals will not be attacked, since some sulphur compounds which may be present in quite small quantities have a greater tendency to attack metals, particularly copper, than others.

The possibility of designing a blue flame wick-fed burner and using this flame to heat an incandescent mantle has long been realized and successful lamps and heaters embodying this principle are now in general use. The successful designing of such a burner is not an easy matter, as very small variations in dimensions of the essential parts of the burner have a very great influence on the flame. The common behaviour of practically all lamps—that of the increase of the size of the flame—accompanied by the risk of smoking, due to the heating up of the metal parts of the burner and the reduction of the viscosity of the kerosine, is a difficulty with which all designers have to contend. The illuminating power of such a burner for a given consumption is much greater than that of the best type of plain wick burner. This is illustrated by the following candle-power determinations on an edeleanized kerosine (no. 3 in Table II, p. 2471) in an incandescent mantle lamp and a circular wick lamp, when burnt at the same consumption:

TABLE XVIII

	Type of burner	
	Incandescent mantle lamp	*Circular wick*
Consumption g. per hr.	69	68
Candle-power (Hefner candles)	76·8	25·7

With incandescent mantle lamps of the blue flame type a high grade of kerosine is essential. A grade which has a high tendency to form char is liable to give a yellow flame in peaks which affect the incandescence of the mantle.

(*c*) Vaporizing Appliances.

Lamps, heating stoves, and cookers employing the principle of vaporizing the kerosine and burning the air-vapour mixture have been developed to a considerable extent, and many successful types of such appliances are now available.

Burners of this type are generally started by preheating by methylated spirit or a blow lamp, before admitting the kerosine to the vaporizer, but devices for starting with kerosine are sometimes used. An important modification of this sytem, consisting of using the vaporized kerosine mixed with air as a gas for heating incandescent mantles, was introduced by Arthur Kitson about 1900.

This system was adopted by Trinity House, who are responsible for the management of British lighthouses, with the result that the large majority of lighthouses which do not have electricity available now use this type of lamp. Such lamps give an intrinsic brightness from 300 to 330 candles per sq. in. of mantle surface.

The figures given below indicate the improvements effected by the introduction of this type of lighting.

TABLE XIX

Type of burner	*Candle-power of flame or mantle*	*Intrinsic brightness per sq. in.*
4-wick (type *a*) .	230	23·6
4-wick („ *b*) .	350	54·43
Mantle („ *a*) .	1,250	156·25
„ („ *b*) .	1,150	328·57

In all appliances of the vaporizing type the kerosine is vaporized by passing through a highly heated vaporizing tube under pressure. The pressure must be adequate to give the stream of kerosine vapour, issuing from a fine orifice at the end of the vaporizer, the necessary velocity to draw into the mixing tube sufficient air to form a gas which, when burning with the secondary supply of air available around the flame, results in a non-luminous flame. These conditions are easily satisfied. Appliances which may be called upon to burn continuously, or even intermittently for long periods without cleaning, call for considerable care in design in order to avoid the clogging up of the fine nozzle with products of decomposition of the kerosine or of its action on the metal walls of the vaporizing tube.

The temperature of the vaporizing tube of such stoves may be about 450° C., that of the lighthouse burners somewhat higher, about 500° C. At these temperatures, especially in view of the very short time that the kerosine is exposed to the heat, cracking does not take place to any appreciable extent. McHatton and Kirby [42] investigated this question by passing kerosine through a silica tube, fitted with a brass liner, heated in an electric furnace at definite rates, and condensing and collecting the issuing vapours by means of a tube cooled to −70° C. A variety of kerosines of various types were examined, ranging from edeleanized paraffin types to highly aromatic types. Up to temperatures of 500° C. all types showed practically no indications of cracking, the condensed distillates having negligible bromine values and no permanent gas being produced. At temperatures round about 575° C. evidences of slight cracking were found, the bromine values of the distillates ranging from 4 to 12, for the kerosines used. At these temperatures only traces of uncondensable gas were evolved. At temperatures of the order of 600° C., however, considerable cracking was evident, condensates with bromine values of from 6 to 20 being obtained and uncondensable gas to the extent of from 1 to 6% by weight. No definite correlation between chemical type and the amount of cracking could be drawn from the number of samples examined.

The absence of appreciable cracking was confirmed by examination of the small quantities of deposits obtained from the vaporizing tubes. These were found to consist largely of sulphides of the metals of which the vaporizing tubes were made.

As the temperatures of the vaporizing tubes of the appliances in general use are well below the temperatures at which appreciable cracking takes place, the fact that so little trouble is experienced in practice from the clogging up of vaporizing tubes is easily explained.

A wide range of kerosines appears to be quite suitable for use in vaporizing burners, the only difficulty with some kerosines being the tendency to corrode the vaporizer tubes.

Owing to the widely differing conditions obtaining in vaporizing burners it is not possible to define the criteria of a satisfactory kerosine for these appliances.

Kerosine for Power Purposes

The use of kerosine as a fuel for internal-combustion engines has increased considerably during the last decade or two. The tendency of consumers to use one type of kerosine for the double purpose of an illuminant and an internal-combustion engine fuel has tended somewhat to retard the development both of engines and of power kerosines. It is, however, now being gradually realized that the characteristics of a good power kerosine differ widely from those of a good illuminating oil, in many cases being diametrically opposed.

The two types of kerosine engines—the hot bulb and the spark ignited—operate on different principles and accordingly require different types of fuel.

Hot-bulb Engines.

In the hot-bulb engine, a compressed charge of fuel and air is ignited by a heated cap or bulb, situated at the top of the cylinder of the engine. In order to start the engine, the bulb must be heated with a blow lamp. After running for some time the heat of compression assisted by the residual heat in the hot bulb is sufficient to ignite the mixture of kerosine and air, the fuel being injected by a pump into the combustion chamber at the beginning of the suction stroke. The compression ratios used are very much lower than those of Diesel engines (about 4 to 1), the actual pressure being about 64 lb. per sq. in., but the fuel requirements, as might be expected, are more in line with those of the Diesel engine than of the gasoline engine. Hot-bulb engines are very sensitive and require adjustment of the bulb temperature to the type of fuel employed. The main factors which determine the suitability of the fuel to the engine are (1) volatility and (2) chemical composition.

1. **Volatility.** A moderately high mean volatility is necessary to ensure complete combustion of the fuel, in view of the relatively low temperatures in the combustion chamber. Generally speaking, kerosines for this type of engine should show about 30% distilling to 200° C. and a final boiling-point not exceeding 300° C.

2. **Chemical Composition.** A high anti-knock value, usually associated with a high spontaneous ignition temperature, is undesirable. The aromatic and naphthene hydrocarbons, which are largely responsible for the high anti-knock value so desirable in a gasoline, are the cause of late ignition in hot-bulb engines. This late ignition results in misfiring and cooling off of the bulb until eventually the engine ceases to fire. On the other hand, a high content of paraffin hydrocarbons, as in the case of

a highly edeleanized kerosine, may cause ignition to take place too early, resulting in over-heating of the bulb and heavy carbonization. It is of the greatest importance, therefore, to suit the fuel to the engine, or vice versa. Generally speaking, a moderately good burning oil of adequate volatility and not too high a final boiling-point will give satisfactory service in a hot-bulb engine. The production of the hot-bulb engine is, however, on the wane, so that fuels specially designed for these engines are not generally available.

Spark-ignition Engines.

Recent developments in the design and flexibility of spark-ignited kerosine engines have led to a great deal of attention being paid to the requirements of these engines; on the other hand, the greater convenience and cheaper running costs of the small high-speed Diesel engine, as compared with the inherent disadvantages and dearer fuel costs of the kerosine engine, may retard the development of both types of engines designed to use this fuel. Much attention has been directed to the conversion of gasoline engines to use kerosine as fuel by the incorporation of heated vaporizers with some degree of success.

There are two main types of vaporizers in common use, viz. (*a*) normal type of dual carburettors, and (*b*) automatic bi-fuel carburettor.

(*a*) The usual vaporizer system possesses separate carburettors for the gasoline and kerosine, while the air intake passes through a manifold heated by the exhaust gases from the engine. The engine is started on gasoline and changed over to kerosine as soon as the manifold is hot enough to heat the air intake to a temperature sufficient to vaporize the kerosine.

(*b*) The use of an automatic bi-fuel carburettor with twin float chambers has the advantage of permitting an increasing quantity of kerosine to be used as the throttle is opened. The engine starts on the gasoline, and is gradually switched over to kerosine automatically as the throttle is opened.

The requirements of kerosine for this type of engine are in general comparable to those of gasoline. The behaviour of a power kerosine in a spark-ignited engine is judged by:

1. Ease of vaporization.
2. Anti-knock value.
3. Lubricating-oil dilution.
4. Consumption.

1. **Ease of Vaporization.** Spark-ignited kerosine engines are generally started up on gasoline, the kerosine fuel being switched on as soon as the engine manifold has become hot enough to heat the incoming air sufficiently to vaporize the kerosine completely. It is therefore essential that the kerosine should have sufficient volatility to pick up from the gasoline starting as soon as possible. The exact volatility requirements will, of course, depend on the efficiency of the heating of the inlet air by the exhaust gases. If the kerosine used is insufficiently volatile, the inlet air must be heated to a higher temperature, thus reducing the volumetric efficiency of the engine. It is generally considered that a power kerosine should have at least 50% distilling to 200° C. A high volatility also increases the flexibility of the engine and facilitates running under light loads.

2. **Anti-knock Value.** In an attempt to improve the efficiency of kerosine engines the compression ratios have been gradually increased, so that in order to keep pace with the fuel requirements of such engines it has become necessary to supply fuels with high anti-knock values.

The anti-knock value of a kerosine is invariably lower than that of a straight-run gasoline made from the same crude, so that power kerosines are generally of much lower anti-knock value than gasolines Fortunately, the improvement of kerosines as illuminants by means of solvent-extraction processes, such as the Edeleanu process, results in the production of an extract relatively rich in aromatics of high anti-knock value, and eminently suitable for the production of power kerosines. Power kerosines, especially if made from crudes mainly paraffinic in character, are thus often improved by admixture with Edeleanu extracts. This convenient fact imparts a considerable degree of flexibility to the manufacture of kerosines of both types. The design of the engine is, however, limited by the knock rating of the kerosines available.

3. **Lubricating-oil Dilution.** The greatest disadvantage of the use of kerosine in an automotive engine is the increased wear on the engine parts caused by dilution of the lubricating oil with incompletely vaporized kerosine. Under conditions of light load, the air intake is liable to be insufficiently heated to vaporize the kerosine completely. For this reason the end-point should be as low as possible, preferably not above 270° C. With engines working under a fairly constant load, such as agricultural tractors, the tendency to dilute lubricating oil is not so great, but it is still a very important factor.

4. **Consumption.** A large part of the power kerosine sold in agricultural districts is packed in tins or drums and sold by volume. A high specific gravity is therefore desirable, as a greater weight of kerosine, and therefore a higher calorific value, is obtained per unit volume, the area ploughed, &c., with unit volume of the kerosine being frequently an important factor in deciding the grade chosen.

REFERENCES

1. Bacon and Hamor. *American Petroleum Industry*, **1**, 116 (New York, 1916).
2. ——— *American Petroleum Industry*, **1**, 121 (New York, 1916).
3. Baker, E. W. Paper read before Institute of Railway Signal Engineers, May 1932.
4. Birch and Norris. *J.C.S.* **110**, 2545 (1926).
5. Borgström, P., Reid, R. W., and Brown, D. F. *A.P.I. Bibliography of Organic Sulphur Compounds* (1930).
6. British Standards Institution, Pamphlet no. 188 (1929).
7. British Standards Institution, Bull. no. 188.
8. Bureau of Mines Tech. Paper 323 B (1927), 68.
9. Carpenter, J. A. *J.I.P.T.* **12**, 555 (1926).
10. Danaila, N. *Petr. Z.* **29** (7), 1 (1933).
11. Danaila, N., and Stoenescu, V. *Petr. Z.* **28** (17), 1 (1932).
12. Danaila, N., Stoenescu, V., and Dinescu, S. *Petr. Z.* **26** (2), 47 (1930).
13. Engler and Levin. *Dingler's J.* **261**, 82 (1886).
14. Groschuff. *Z. für Elektrichemie*, **17**, 348 (1911).
15. Grote, W., and Hundsdörfer, E. *Petr. Z.* **28** (28), 9 (1932).
16. Hillman, E. S. *Proc. World Petr. Cong.* **2**, 708 (1933).
17. Holde. *Kohlenwasserstofföle und Fette*, 38 (Berlin, 1924).
18. —— *Kohlenwasserstofföle und Fette*, 18 (Berlin, 1933).
19. —— *Kohlenwasserstofföle und Fette*, 229 (Berlin, 1933).
20. —— *Kohlenwasserstofföle und Fette*, 342 (Berlin, 1935).
21. Jackson, J. S. *Proc. World Petr. Cong.* **2**, 669 (1933).
22. Jones and Wootton. *J.C.S.* **91**, 1146 (1907).
23. *J.C.S.* **52**, 1239 (1930).
24. Kewley, J., and Jackson, J. S. *J.I.P.T.* **13**, 371 (1927).

25. Leslie, E. H., Geniesse, J. C., Legatski, T. W., and Jagrowski, L. H. *Ind. Eng. Chem.* **18,** 45 (1926).
26. Mabery, C. F. *J.S.C.I.* **19,** 502 (1900).
27. —— *J.S.C.I.* **19,** 502 (1900).
28. Mabery, C. F., and Hudson. *Amer. J. Science,* 1894, 250.
29. Mabery, C. F., and Quayle. *J.A.C.S.* **28,** 404 (1906).
30. Mabery, C. F., and Smith. *Ber.* **22,** 3303 (1889).
31. McHatton, L. P. *Proc. World Petr. Cong.,* **2,** 721 (1933).
32. Minchin, S. T. *J.I.P.T.* **17,** 102 (1931).
33. —— *Proc. World Petr. Cong.,* **2,** 738 (1933).
34. Minchin, S. T., and Nixon, G. R. *J.I.P.T.* **14,** 477 (1928).
35. Moerbeek, B. H., *Proc. World Petr. Cong.* **2,** 704 (1933).
36. —— *Proc. World Petr. Cong.* **2,** 713 (1933).
37. Mulany, H. M., and Watson, E. R. *J.S.C.I.* **43,** 310 T (1924).
38. Nakamura. *J.S.C.I.* **2,** 535 (1883).
39. von Pilat, Sereda, and Szankowski. *Petr. Z.* **29** (3), 1 (1933).
40. Poth, E. J., Armstrong, W. D., Cogburn, C. C., and Bailey, J. R. *Ind. Eng. Chem.* **20,** 83 (1928).
41. Private communication.
42. Private communication.
43. Rather, J. B., and Beard, L. C. *Refiner,* **15,** 217 (1936).
44. Redwood. *Treatise on Petroleum,* **1,** 275 (London, 1922).
45. Rossini, F. D. *Oil and Gas J.* **33** (52), 61 (16 May 1935).
46. Sachanen and Telicheyev. *Petr. Z.* **23,** 521 (1927).
47. *Standard Methods for Testing Petroleum and its Products,* Institution of Petroleum Technologists, 3rd ed. (London, 1935).
48. *Standard Methods for Testing Petroleum and its Products,* Institution of Petroleum Technologists, 3rd ed. p. 200. Serial Designation K 35 (I) (London, 1935).
49. Stepanoff. *Grundlage der Lampentheorie* (1906).
50. Story, L. G., and Snow, R. D. *Ind. Eng. Chem.* **20,** 359 (1928).
51. Tasaki and Yamamoto. *J.S.C.I.* (*Japan*), **34,** 247 (1931).
52. Terry, J. B., and Field, E. *Ind. Eng. Chem.,* Anal. Ed. **8,** 293 (1936).
53. U.S. Bureau of Standards Misc. Pub. no. 97. *Thermal Properties of Petroleum Products,* 29.

LIGHT DIESEL FUELS

By G. D. BOERLAGE, *Director, Proefstation Delft,* and J. J. BROEZE, *Exp. Engineer, Proefstation Delft*
in collaboration with
AMSTERDAM RESEARCH LABORATORIES OF THE ROYAL DUTCH SHELL

I. INTRODUCTION

UNDER this heading are comprised fuels for small Diesel engines, for high-speed engines, for semi-Diesel engines, &c., and, generally speaking, for such engines as are somewhat particular as to their fuel, on account of poor design, &c.; it comprises also fuels for big or slow-speed engines in cases where fuel cost is of secondary importance against features like ease of starting and extreme reliability (peak load and emergency sets). Even spark-ignition engines, either simply of the carburettor type or of the injection type, have to be considered. The name 'light Diesel fuel' therefore refers more to its easy use in engines than to low specific weight, low boiling range, low viscosity, &c.

The principal characteristics of these engine types will be explained in a few words, in order to understand their different requirements.

(*a*) Compression-ignition Engines (C.I. Engines).

Air only is aspirated and compressed to a high pressure and temperature (volumetric ratio 1:13–20). Fuel is injected near T.D.C. under high pressure and atomized. Combustion starts owing to self-ignition, usually when only a small part of the spray has been introduced. Therefore, the chance of fuel coming into contact with cold walls is relatively small; nevertheless this may happen, especially in small engines or in engines with neglected nozzles.

(*b*) Hot-surface-ignition or Akroyd Engines.

These work on nearly the same principle, but the compression ratios are lower (1:7–10), so that for maintaining ignition use is made of uncooled parts of the combustion chamber walls, which assist evaporation and ignition. The spray device may be much cruder than that of the C.I. engines, as the uncooled parts, assisted by some turbulence, take charge of evaporation and distribution. Ignition is usually self-ignition; sometimes the injection is very early, in which cases a considerable ignition lag is required to avoid too early ignition; in some cases flame ignition resulting from hot gases of a previous cycle is relied upon; then the injection can be later and the danger of pre-ignition is less.

(*c*) Spark-ignition Carburettor Engines.

In this class of engine it is sometimes attempted to burn heavier fuels than power kerosine. Fuel and air are mixed outside the cylinder, with preheating arrangements, in order to obtain a stable mixture of fuel and air. The mixture is aspirated and compressed (volume ratio 1:4), then fired with a spark. Preheating may cause gummy deposits in the induction system. As the mixture is for a long time in contact with engine walls, there is a danger of condensation, causing, for instance, dilution of lubricating oil. Self-ignition must be avoided (detonation), which is an exigency contrary to that for a Diesel fuel and which makes the use of light Diesel fuels for such engines a doubtful compromise, although attractive because of the lower price.

(*d*) Spark-ignition Injection Engines (Hesselman low-pressure type).

Air is again introduced separately and a low compression ratio is used (1:5–7). The fuel is injected near the end of compression and is ignited by an electric spark. The time for contact between fuel and engine walls is still slightly longer than with C.I. engines. Again self-ignition must be avoided, but since the fuel is only partly injected at the time of ignition, there is not much chance of self-ignition or detonation occurring.

Table I gives the above types of engine with their fuel requirements in principle.

TABLE I

Fuel requirements	*Engine types*			
	Compression ignition	*Hot-surface ignition*	*Spark ignition*	
			Carburettor	*Injection*
Volatility	Rather unimportant	Rather important	Very important	Rather important
Ignition quality	Rather important High	Important, but depends on type	Important Low	Rather important Low
Viscosity	Rather unimportant Not too low	Rather unimportant Not too low	Important	Rather unimportant Not too low
Tendency to form gum	Not important	Not important	Very important	Not important

The conditions for a light Diesel fuel are adequately met by the fuels called *gas oil* or *solar oil* in Europe and eastern countries, and by *stove oil* or *light furnace oil* in the U.S.A.

The main requirement of such a fuel is the absence of constituents of low volatility, which may be harmful to combustion efficiency, when contact of the fuel spray with the walls of the combustion chamber cannot be avoided (particularly in small high-speed engines) and when the nozzles are prone to carbonization (overheating, poor design). Particularly the percentage of asphalt should be very low. Some crude oils do not contain such asphalts by origin; others are freed of asphalt by distillation or some other means.

The viscosity of light Diesel oils should not be too low, neither too high, as the small high-speed units as a rule are not equipped with a device to preheat their fuel before it passes the last filters and the injection pumps and nozzles, but with fuels free from asphalt the upper limit of viscosity is scarcely reached in practice.

The fuel is not further refined chemically, like petrol or lamp oils. As it is practically not exposed to air under oxidizing conditions until its introduction in the cylinder, refining in order to remove products likely to develop gummy matter appears to be superfluous.

Part of the pressure distillate obtained at the cracking plants is sometimes used also as a Diesel fuel, either singly or blended with straight-run distillates. The cracked material is distilled and thereby divided into the cracked residue and the pressure distillate. The latter is fractionated in order to take off the cracked petrol fractions; the remainder, the *pressure distillate bottoms*, is either used as recycling stock or, if its further yield of light fractions is unsatisfactory, it is taken out of the further process and used, for instance, as a light Diesel fuel, as it has suitable properties.

In particular in the U.S.A. the larger part of light Diesel fuels consists of this material, as straight-run gas oils are too valuable a charging stock for cracking operations. As the P.D. bottoms have been once or more through the cracking apparatus, they have some particular characteristics that may cause them to differ from most straight-run oils. We refer firstly to the fact that the prolonged exposure to high temperatures has diminished the content of easily decomposable constituents, which lowers the ignition quality somewhat. However, a cracked oil from a certain crude may still be higher in ignition quality than the straight products from another crude. Furthermore, with highly cracked products, the content of unsaturated compounds, in particular those which tend to form gums, may be so high that on storage gum may be formed, causing difficulties with filters and the injection apparatus. For such products, therefore, further refining may be necessary. Large quantities of P.D. bottoms are, however, used quite successfully. Pressure distillate bottoms such as Diesel fuels are frequently used in oil-less countries which have prohibited or restricted the import of finished petroleum products, and in those countries, therefore, extensive cracking plants are found for the manufacture of petrol and other distillates.

Owing to their lower volatility range the light Diesel fuels have a considerable advantage over the lower boiling fuels (such as motor spirit and kerosine) from the point of view of fire hazard. In this connexion all civilized countries have legislation covering the storage and transportation of the lighter fuels. As a rule the criterion applied to determine whether a particular fuel is to be regarded as hazardous or not is a so-called 'flash-point' test, which consists in determining the lowest temperature at which the liquid, when tested in a particular form of apparatus under standardized conditions, yields an ignitable air-vapour mixture. The method followed and the instruments employed unfortunately differ in various countries. As examples we may cite for kerosines: the Tag Closed tester (A.S.T.M. Method D. 56–21), as employed in the U.S.A., the Abel method employed in Great Britain (Petroleum Act, 1926), the Abel-Pensky method which is followed in Germany (Physikalisch-technische Reichsanstalt, Berlin, 1913) and several other European countries, and the Luchaire test of the French Customs. Although, as stated, the flash-point was primarily intended purely as a measure of fire hazard, it has in the course of time become usual to apply a similar test also to the higher-boiling oil fractions, even if they are obviously non-hazardous. The methods applied in this case comprise: the Pensky-Martens closed cup test (I.P.T. Standard Test, A.S.T.M. Standard D. 93–22), and the Cleveland open cup test (A.S.T.M. D. 92–33). These tests are frequently regarded as giving a certain measure of the volatility of the material (and hence an indication of its origin), but it is obvious that it is preferable to determine volatility directly by some standardized distillation procedure (see below). The flash-point gives no information as to the burning properties of the fuel.

II. PHYSICAL AND CHEMICAL CHARACTERISTICS

In the following the principal physical and chemical characteristics of light Diesel fuels are discussed with respect to the practical significance thereof.

(*a*) Distillation Range.

The volatility or distillation range of light Diesel fuels is usually determined by a standard distillation test. The use of the method introduced by the American Society for Testing Materials (A.S.T.M. Standard Method D. 158–28) is very widespread, although some countries still employ other procedures (e.g. the Luynes-Bordas method of the French Customs, *Journal Officiel*, 17 Nov. 1926). It should be realized that all such tests give entirely conventional results, the distillation curve obtained being always an intensely 'smoothed-out' version of the actual boiling-point percentage graph, owing to the very low degree of fractionation present.

Table II gives some figures obtained with the A.S.T.M. distillation method on three typical light Diesel fuels.

TABLE II

	Initial b.p.	*10*	*20*	*30*	*40*	*50*	*60*	*70*	*80*	*90*	*Final b.p.*	*% off*
Gas oil (1)	228	254	263	271	279	288	298	320	322	341	362	95
,, (2)	202	225	232	239	247	256	267	279	298	325	350	95
Distillate (3)	221	272	290	307	324	338	354	370	..	..	375	74

These results illustrate the influence of the method of manufacture on the character of the fuel. Gas oil (1) is a product obtained after removal of a portion of the kerosine fraction; gas oil (2) is a light Diesel fuel made without kerosine production (as indicated by the lower initial boiling-point); whilst distillate (3) is a product with a considerably higher final boiling-point, owing to the fact that it was obtained in distilling down to a bitumen.

For high-boiling fractions, over about 370° C., the A.S.T.M. or similar distillation tests are not reliable, as cracking sets in, due to the long heating time, during which the temperature of the liquid is still higher. This is also serious inasmuch as heavy distillates cannot be readily distinguished in this way from fuels blended with heavy residue. Cracking during the distillation test results mainly in an increased percentage distilled, as light fractions are formed, and in the formation of carbonized residue in the flask. The formation of low-boiling cracked products, if serious, is usually noticeable by the discontinuity of the distillation curve, to which Sass [19, 1935] has again drawn attention. Coke is formed during distillation; it must be emphasized that this coke is a product of the destructive process in the distillation flask and that it has no direct bearing on the behaviour of the fuel in the engine, notwithstanding opinions to the contrary (Lunge-Berl [12, 1921]). The occurrence of decomposition during distillation may, on the contrary, point to the presence of paraffinic hydrocarbons of good ignition quality; when the phenomenon occurs, it is not justifiable to connect it with bad burning qualities or even abnormal cylinder wear (Sass, ibid.).

The curve obtained by an A.S.T.M. or similar distillation test is, as already stated, a conventional measure of the volatility range of the fuel, its shape being determined by the relation between the composition of the vapours in equilibrium with the boiling liquid at any stage of the distillation and the small degree of fractionation present. In the case of the lower-boiling fuels (motor spirit and kerosine) it was at one time usual to determine the so-called 'dew-point', as this is more closely related to conditions during carburation. (The dew-point is the temperature at which vapours at atmospheric pressure of a totally volatilized liquid are in equilibrium with the first trace of condensed liquid.) It was found, however, that the dew-point, in the case of these lower-boiling fuels, usually coincides fairly accurately with the 65 vol. % point on the A.S.T.M. distillation curve, and the direct determination of the dew-point is now seldom carried out. The relation between the dew-point and the course of the distillation curve is not known in the case of a Diesel fuel, and at all events it is doubtful how its influence on the evaporation process in the Diesel engine should be interpreted. The conditions in a Diesel engine are, of course, quite different from those during the distillation test, the air-pressure being of the order of 30–40 atm. at the moment of injection, whereas the vapour-pressure of the fuel, starting at zero, reaches some 0·3 atm. after evaporation of a full charge of fuel, where this is evenly distributed. Locally, due to uneven distribution, vapour-pressures may be much higher. Still, some such point as the dew-point might be of use for determining the relative ease of complete evaporation.

About the influence of volatility of the fuel on combustion opinions appear to differ widely. Moore [14, 1928] and Le Mesurier and Stansfield [10, 11, 1931–32] are of the opinion that it is of no influence on the behaviour of the fuel and may only serve to identify the fuel to a certain extent. Sass was of the same opinion [18, 1929], but does not wish to maintain this opinion now [19, 1935], since he found various troubles with incomplete combustion or undue carbonization, which he ascribes to oils of unsuitable volatility. Since the fuels considered by Sass included fuels containing large amounts of asphaltic residue, there is no contradiction, if the authors suggest that for the light fuels the influence of volatility is usually beyond detection. Under average conditions of load it is not possible to find any difference in fuel consumption or even in carbon deposit between fuels of widely different volatility. Actually in combustion chambers which are prone to over-penetration of the fuel a lower boiling range is of some advantage, as it assists in evaporating quickly the deposits of over-penetrated fuel; on the other hand, if the engine is prone to under-penetration, too volatile a fuel makes the effect thereof worse; these effects are usually only noticeable near the power limit of the engine. It is evident that the over-penetration leads more readily to carbon formation, but the under-penetration with as a result a dirty exhaust may be as harmful from the point of view of piston troubles. A fact which makes the analysis of the effect of volatility in this respect difficult is that the 65% distillation points of distillate fuels correlate to some extent with viscosity, so that any effect of viscosity on penetration will be enhanced by a corresponding volatility effect (Fig. 1).

(*b*) Specific Gravity.

The specific gravity of hydrocarbons varies with their chemical nature and their molecular weight. For light distillate fuels it varies, therefore, also with their nature and with the boiling range. The members of the paraffinic and olefinic series have the lowest specific gravities, the cycloparaffins or naphthenes somewhat higher, and the aromatic ring compounds the highest. Whilst specific gravity has, of course, no meaning by itself as to the behaviour of the fuel, it may give some indication about the chemical type of the fuel, if considered together with the boiling range. Even then a mixture of paraffinic compounds with aromatics may have the same specific gravity as a mixture of naphthenic compounds; further information can then be obtained only after chemical analysis.

In practice the specific gravity of light Diesel fuels may vary between 0·82 and approximately 0·93, the lower limit being represented by those fuels containing a minimum of naphthenic and aromatic and a maximum of paraffinic compounds or groups, whilst the oils of high specific gravity, on the other hand, are those rich in naphthenic and aromatic compounds or groups. The only importance of the specific gravity in practice, apart from identification of a fuel, lies in the rough relation between the chemical composition and the ignition quality of the fuel (vide Ignition Quality Indices on p. 2493). In the U.S.A. it is customary to express specific gravity as A.P.I. gravity degrees, for which the conversion formula is the following:

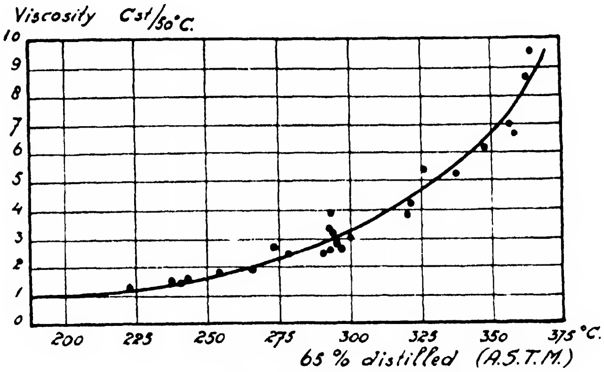


FIG. 1. Viscosity-volatility correlation.

$$°\text{API.} = \frac{141\cdot5}{\text{Sp. gr. } 60°/60° \text{ F.}} - 131\cdot5; \text{ A.S.T.M. D. 287–33.}$$

(*c*) Viscosity.

Viscosity should be expressed in units of kinematic viscosity; at the World Petroleum Congress [17, 1933] a resolution was passed to that effect. The practical unit of absolute viscosity is the centipoise, that of kinematic viscosity (relating to the rate of laminar flow under a head of liquid and equal to the absolute viscosity divided by specific gravity) the centistoke. Kinematic viscosity can be determined with the B.S.I. (British Standard Method 188) and with the Vogel-Ossag viscometer (Erk [4, 1927]).

In practice there are in use a variety of instruments (Engler, DIN DVM 3655; Redwood, I.P.T. Serial Designation L.O. 8; Saybolt, A.S.T.M. Designation D. 88-36; and Barbey Ixometer) in which viscosity is measured by taking the time of outflow of a certain quantity of liquid. The relation between the values obtained on these instruments and kinematic viscosity is given elsewhere. It is seen that especially in the area of light Diesel fuels these instruments become gradually less sensitive, due to the beginning of turbulence of the outflow. Now for these fuels viscosity is of small importance, since it is always low enough to ensure efficient atomization as well as easy transportation and handling, and the only point usually raised is that the viscosity should be high enough to ensure a reasonable sealing of the fuel-injection system, and for this purpose only a direct measurement in centistokes or centipoises can serve. The only viscometers giving exact figures in this region are the above-mentioned B.S.I. and Vogel-Ossag instruments, in which, by means of special capillary tubes, the outflow is kept in the region of laminary flow. Fuel pumps and injectors are made with the moving part (pump plunger or needle valve) a lapped fit without any packing in the guide, and under the high pressures used for injection (100–500 atm.) a certain amount of leakage will always occur, which is a function of the fit, the construction and the pressure on one hand, the viscosity on the other. Le Mesurier and Stansfield found that the leakage was inversely proportionate to the kinematic viscosity of the oil [10, 1931]. The pump leakage, in itself, is not important, since usually provision is made to recover the oil lost; modern fuel valves leak so little that it is not considered necessary to recover the oil, leakage being conducted to waste. The real trouble is that with too much leakage the control over the rate and the quantity of injection is lost; in particular this may be the case with fuel pumps employing slide valves (Fig. 2), where the sealing length is very small indeed. The leakage takes place in that case towards the suction side of the pump, so that no oil is actually lost. Only high-class workmanship has made possible the great success of this type of pump.

Minimum values such as 4·5 centipoises (abs. visc.) or 5 centistokes (kinematic visc.) at 20° C., 35-sec. Redwood or 42-sec. Saybolt at 100° F., or 1·2° Engler at 20° C. are sometimes found in fuel specifications, in order to limit this leakage; these values correspond very well with each other, but it must be kept in mind that the temperatures specified are merely those convenient for viscosity determination, and serve only as an indication of the fuel's viscosity, which changes with temperature. Fig. 3 gives the viscosity as a function of temperature for some light fuels and shows at the same time at what engine temperatures these fuels are used in practice. The variation of viscosity with pressure (Hersey [7, 1929]) is not usually taken into account.

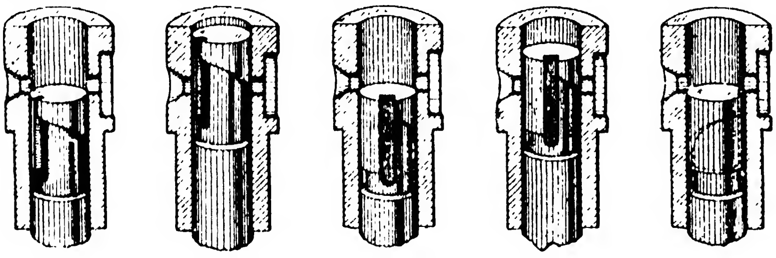


FIG. 2. Five positions of the plunger of a fuel pump.

The maximum admissible value for viscosity of light fuels is a matter of engine design, but practically the question is of little importance, since light fuels with viscosities over 25–30 *Cp*/20° C. are very scarce, while fuels of this viscosity do not cause any trouble in high-pressure injection systems of C.I. engines; it may be too high for the simple sprayers of Akroyd engines, for which some preheating may be necessary. The low-pressure metering system of carburettors is unfit for dealing with such liquids because of the variation of viscosity with temperature.

(*d*) Chemical Composition.

As has already been stated, light Diesel fuels may be regarded as being mainly composed of hydrocarbons consisting of paraffin chains, naphthenic rings, and aromatic rings. In the order given these constituents show a diminishing hydrogen and an increasing carbon content. In practice the carbon content of a light Diesel fuel varies between approximately 86 and 89%, the hydrogen content between 10 and 13%. The products always contain a certain percentage of sulphur compounds (the sulphur content usually varies between 0·2 and 2%) and up to 1% of other elements (oxygen, nitrogen, &c.).

Chemical methods of separating the various groups of compounds and of determining the percentage in which they occur are of doubtful value in the case of such low-boiling petroleum fractions as occur in motor spirits, and may be said to be extremely doubtful and therefore practically useless in the case of the higher fuel fractions. This is due to the fact that substitution becomes very much more probable as the molecular weight increases; in other words, it is due to the fact that aromatic compounds with paraffinic side chains, aromatics combined with naphthenic rings, naphthenic rings with side chains, or compounds containing all these constituents undoubtedly do occur.

A method of analysis which seems to offer considerable promise is that developed by Professor H. I. Waterman and collaborators [23, 1932]. This method does not aim at determining the percentage of compounds, but of the three above-mentioned constituents of the compounds, viz. the paraffinic chains, naphthenic and aromatic rings. The actual procedure cannot be described here, but it is based on the determination of the specific refraction and the average molecular weight of the material before and after a complete hydrogenation, by which means the aromatic nuclei are completely reduced to the corresponding saturated rings. A graph, calculated from the well-known specific refraction data of Eisenlohr, permits the hydrogenated oil to be expressed as containing a certain 'average number of rings per molecule', whilst the amount of hydrogen consumed during hydrogenation is a measure of the amount of aromatic rings in the original oil. (The original method can only be employed when olefines are absent, as can be determined by the bromine number.)

The elementary analysis can serve only for the distinction of highly aromatic fuels from others, and for an approximation of the calorific value. It does not lead to a conclusion about the ignition quality, which is dependent on molecular structure. Even the division into the main groups stated above is insufficient for that purpose, as, for example, straight-chain paraffins or olefines and corresponding isomers may behave quite differently (Boerlage and Broeze [2, 1932]). The ignition quality must at present be determined experimentally. By reason of the fact that natural petroleum fuels do not appear to contain all the possible hydrocarbons within their boiling range, some relationship between ignition quality and their chemical character (made evident by specific gravity, aniline point, &c.) may be used to some extent as an ignition index (vide p. 2493), which, however, fails as soon as other, e.g. synthetic, hydrocarbons are taken. Apart from the influence on ignition the chemical composition of the fuel has not been found to be of any practical importance for its combustion. The velocity of combustion after ignition has not been found to be influenced by the composition of the fuel (vide *Combustion Research in C.I. Engines*, part iii, p. 2902). The differences in composition have a slight effect on the amount of oxygen required for combustion, but for Diesel fuels this is inside the limits of the irregularity with which the combustible mixture is obtained in the engine.

Apart from the main composition the following details thereof may be of interest.

Sulphur, which may occur up to some 2%, is present in various forms. The effect in practice of such small percentages is very small; though undoubtedly corrosive acids are formed by the combustion of sulphur, which may attack the metals with which the flame gases come into contact under suitable temperature conditions, general experience is that no serious harm ensues. Moore [14, 15, 1928–35] warns against sulphur as an indication of hard asphalts, which is of interest for heavy residual fuels only.

Oxygen may be present mainly in the form of acids. The organic acids found are mostly those occurring naturally in petroleum, bearing the name of naphthenic acids; fatty acids are scarcely found, as are also phenolic acids, which are present in coal-tar oils. In certain naphthene base oils the acid value, expressed in mg. KOH/1, may go up to 2, although 1 is a better average for this type of oil. Naphthenic acid is relatively harmless for metals, especially steel of which the polished pump parts are made. Copper is stained in the long run, but not in a measure to endanger the copper oil pipes. The only inconvenience with naphthenic acid is its affinity for softer metals like zinc, which gives rise to difficulties when galvanized containers are used. The formation of metal soaps obstructing fuel filters and the presence of zinc-oxide formations in the combustion chamber (pale yellow deposit) have been observed. Mineral acids are not encountered. *Asphalts* are complex compounds of extremely low volatility and therefore should not be found in a light fuel. 'Soft' asphalt such as is determined by the alcohol-ether test (Holde [8, 1933], p. 168) may go up to 1%; it is generally agreed that this kind of asphalt does not influence the combustion process. Moore [14, 1928; 15, 1935] leaves it out of the specification altogether. 'Hard' asphalt, such as is determined by methods employing low-boiling aromatic-free spirit, e.g. the test of the I.P.T. (Method A. 12) or the di-ethyl-ether test (Everett [5, 1934]), is usually considered to cause difficulties with combustion when present in large quantities (Moore [14, 1928; 15, 1935], Sass [18, 192); 19, 1935]).

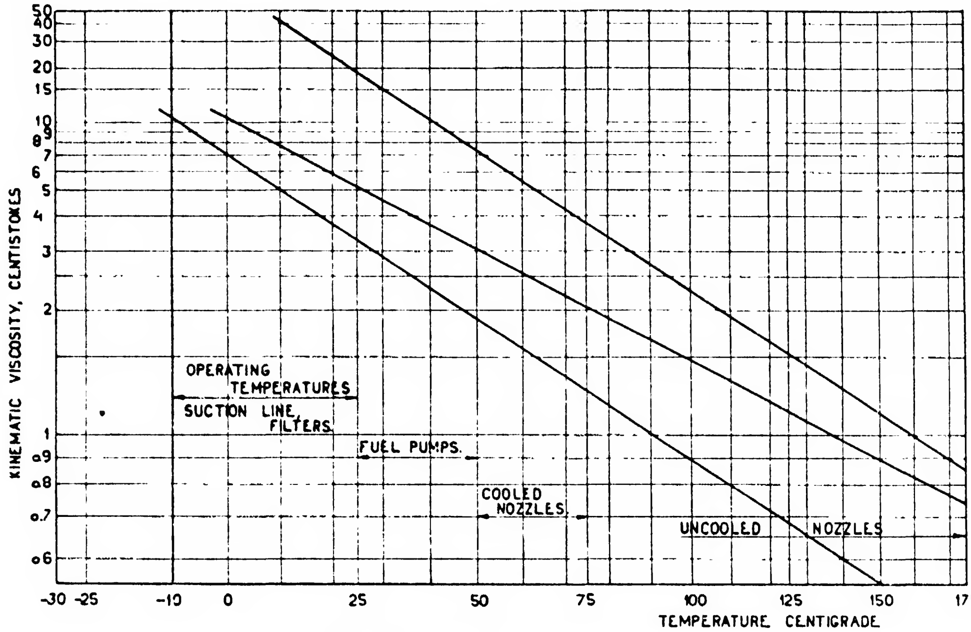


FIG. 3 Viscosity temperature graph.

Yet, with suitable construction of the engine, it may be burnt well. The light fuels of the types specified usually contain only about 0·1%.

Unsaturated compounds may be determined by the bromine value (McIlhiney method [13, 1920]). Their presence mostly indicates that the fuel contains cracked products. Apart from this fact it is of no great interest. Bromine numbers up to 15–20 have been met with in fuels giving entire satisfaction.

(*e*) Calorific Value.

The calorific value is mainly dependent on the chemical composition of the fuel, as the calorific value of the main constituents, hydrogen and carbon, differs widely. When determining the calorific value of a hydrocarbon in a bomb (Holde [8, 1933], p. 80), the water formed is condensed practically entirely, whereas in an engine the gas temperatures remain so high that there is no question of condensation. As condensation of water vapour yields the high latent heat (about 600 kg.-cal./kg.), this may make an important difference. The continental practice is to reckon with the lower or net calorific value, i.e. the calorific value obtained from the bomb test (gross value) corrected for the condensation heat. The gross calorific value generally increases with the hydrogen content, but the latent heat of the increased quantity of water offsets this increase to a large extent. The following values are taken from the table by Le Mesurier and Stansfield [10, 1931]:

TABLE III

Composition and Heat Value of Distillate Fuels

Fuel no.	C	H	S	Sp. gr. 60° F.	Heat value		Type
					Gross	Net	
1	85·6	12·7	1·07	0·867	19,500	18,290	Mainly paraff.
5	85·6	13·0	0·54	0·833	19,700	18,460	Shale (paraff.)
6	85·7	12·7	0·85	0·852	19,800	18,600	Mixed, mainly paraff.
7	86·5	12·8	0·11	0·867	19,700	18,490	Naphthenic
8	85·4	12·8	0·63	0·855	19,675	18,460	Naphthenic
10	86·8	11·6	0·50	0·904	19,150	18,050	Naphth.-arom.

The largest difference in net heat value here is 3%.

When stating the fuel consumption of an engine it is customary to refer to a normalized fuel. Continental practice is to refer to a fuel of a net or lower heat value of 10,000 kg.-cal./kg. (18,000 B.Th.U./lb.), whereas British practice is to refer to a fuel of a gross value of 10,750 kg.-cal./kg. or 19,350 B.Th.U./lb. (British standard specification).

(*f*) Paraffin Wax.

Paraffin wax may be in solution in distillate fuels. Its only inconvenience is that at low temperatures it will crystallize out, at first in small crystals which may cake on fine filters and obstruct them, whilst at still lower temperatures the flow of the fuel under low pressure is impaired, so that suction of the fuel pumps is interrupted. The first temperature at which flocculation of wax will occur after a certain time is called the cloud-point, for which no specified method exists; the lower temperature at which flow under specified conditions is interrupted is the pour-point (A.S.T.M. Method D. 97–28). Somewhat dubious is the name 'cold test', which may mean either the one or the other, whereas cloud- and pour-points may differ entirely according to the type of oil. Separation of wax may occur in a certain fuel and cause filter troubles, but the total wax content may be insufficient to form a wax skeleton impairing flow at all. In practice, when fine filters are used the fuel can be utilized down to the cloud-point, as usually the filters are placed beside the engine and assume the temperature of the surroundings. In some installations where the filters are heated by the engine or where gauze filters are applied, the fuel can be used without difficulty, even at lower fuel temperatures. Near the pour-point the flow of the fuel becomes unreliable, in the many cases where the head is insufficient. Preheating is then necessary.

(*g*) Foreign Matter.

Water, sand, dust, fibrous matter, iron, or other oxides mainly find their way into the fuels between the refinery and the engine, and they must be removed in order not to impair the proper working of the injection system.

Water, apart from accidental big quantities, is usually found in the form of very fine suspensions. Temperature differences as between day and night cause breathing of the air space in the oil container (tank, drum) and may also cause condensation of some water, especially in winter; the water settles as a fine white fog on the surface, and after some time it is entirely dispersed through the oil, which becomes opaque. This form of water is objectionable in that it blocks up non-metallic filters, and it may cause some corrosion of pump parts. The difficulty is mostly found in drums which have not been hermetically sealed. This or ventilating, such as can be done in tanks, is the only remedy. Besides the solid impurities which are introduced by obvious causes usually during filling operations, in particular iron oxide may be mentioned, which occurs in the form of scale from blue iron drums. For these very small particles metal filters appear to be insufficient, unless they are of the ultra-fine type (Lolos, Hesselman). Good results have been obtained by taking the fuel from the drum through a filter consisting of a pad of cotton waste between two sieve plates.

III. BURNING CHARACTERISTICS

For fuels relying on self-ignition for their burning the *ignition quality* is of great importance. This quality is the relative tendency of fuels to ignite, preferably under engine conditions. For indicating the readiness to give complete combustion of the fuel it has been tried repeatedly whether a *combustion quality* could be just as easily defined and measured; this, however, is not the case. For the completeness of combustion so much depends on the formation of the mixture, i.e. on the construction of the engine, that the same fuel characteristics may at one time be advantageous, and at another time not so (vide *Combustion Research in C.I. Engines*, p. 2894—influence of viscosity and of evaporation on mixture).

Ignition Quality (for ignition in Diesel engines vide *Combustion Research in C.I. Engines*).

Good ignition quality promotes easy starting and regular ignition, early enough to avoid knock from accumulated fuel. However, it should be well understood that good engine design is at least as powerful a factor in this respect.

(*a*) Spontaneous Ignition Temperature.

Early investigations had shown that the coal-tar oils, which were notoriously difficult to burn in Diesel engines, had higher spontaneous ignition temperatures (S.I.T.) than petroleum fuels. These S.I.T. values were determined by letting a drop of the fuel fall into a heated crucible (Holm [9, 1913], Moore [15, 1935] and noting the lowest temperature at which an explosion would occur. Fig. 4 shows the apparatus used by Wollers and Ehmcke [24, 1921] and known as the Krupp ignition tester, which is a development of the earlier apparatus. (Vide Chaloner in the Symposium on Spontaneous Ignition Temperatures held for the I.P.T., 1932 [21*b*].)

In the ignition testers oxygen was usually employed, slowly scavenging the crucible, as it was felt that a higher oxygen concentration than the atmospheric gave a better approximation to the high air density in the engine; moreover, the explosions when using air were often rather indistinct. From the tables of results obtained (Table IV) it is seen that considerable differences are found between petroleum fuels and other products, but that less difference is found among petroleum fuels mutually.

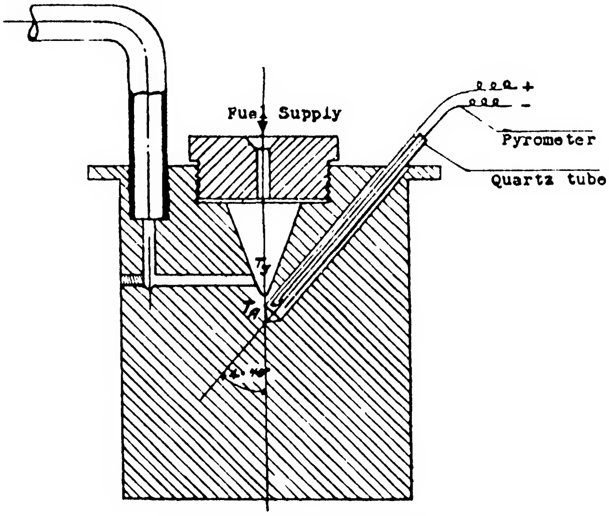


FIG. 4. Krupp ignition block.

At that time this was of secondary importance, as the engines were low-speed air-injection engines rather insensitive to ignition quality; the advent of high-speed solid-injection engines in later years placed the problem in an entirely new light and necessitated a much finer distinction being made.

TABLE IV

Spontaneous Ignition Temperatures in Oxygen (Holm)

Tar oil	530° C.
Benzene	520° C.
Ethyl alcohol	510° C.
Hydrogen	470° C.
Petrol	415° C.
Compressor lubricating oil	410° C.
Petroleum kerosine	380° C.
Roumanian fuel oil	380° C.
Lignite kerosine	370° C.
Gas oil	350° C.

Tausz and Schulte [22, 1924], in a very comprehensive work on the subject, detected certain anomalies between the S.I.T. taken in air and that taken in oxygen, and proposed to determine it in air under pressures more nearly equal to those occurring in engines. Various apparatus were worked out by them to that end. In particular they observed a case where mixtures of a petroleum or brown coal product (having a low S.I.T.) with a coal-tar oil, when tested under pressure, had S.I.T. values higher than that of the tar oil alone, which led them to the conclusion that such mixtures would be more difficult to ignite in the engine than the tar oil. Now such a behaviour has never, to the authors' knowledge, been observed in engine tests, where mixtures always show an increase in ignition lag with increasing percentages of coal-tar oil or other substances of the same character. This shows that measurements of the S.I.T. cannot always be directly translated into engine performance. Still later an elaborate S.I.T. determination was worked out by Jentzsch (Symposium [21*b*]), who found that fuels may have two S.I.T. values, a lower and a higher one, with a peculiar area between them, in which the occurrence of ignition was dependent on the velocity of admission of oxygen (Fig. 5). The apparatus consisted of a steel block with three interconnected receptacles, into one of which the fuel was admitted (Fig. 6). Up to now it has not been possible to obtain more than a rough correlation between one of the numerous 'indices' proposed by Jentzsch and ignition determinations made on the engine.

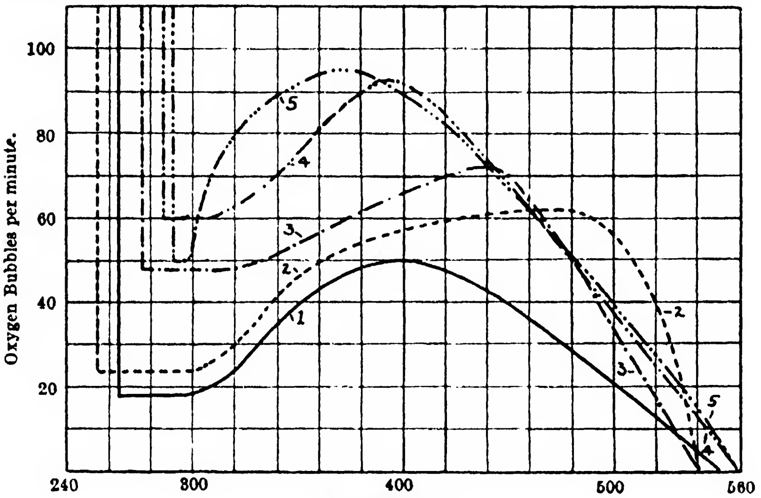


FIG. 5. Jentzsch curves. 1. Russian Diesel oil. 2. Roumanian special power kerosine. 3. Gas oil, origin unknown. 4. Gas oil, origin unknown. 5. Lignite fuel oil.

(*Reproduced by permission from Journal of the Institute of Petroleum Technologists*, **18** (1932).)

(*b*) Ignition Lag.

Hawkes [6, 1920] had already drawn attention to the fact that at temperatures above the S.I.T. there always remained a certain time lag before ignition sets in, and that for working conditions this lag was more important than the lowest temperature at which ignition would occur. The first systematic investigations into the ignition lag confirmed this in so far that fuels with very little difference in S.I.T. would still have appreciably different lags in an engine (Le Mesurier and Stansfield [10, 1931], Boerlage and Broeze [1, 1931]). It was felt then that until more experience had been gained measurements of ignition quality could best be made in the engine itself or under conditions very closely approaching those in the engine. Obtaining ignition values in an apparatus has always the advantage that temperature and composition of the air charge are known exactly, and, moreover, it is hoped that the expenses of installing and operating the apparatus might be lower than those of a special engine. Against that the engine gives the most direct answer (provided that correlation exists between different engines), has so far appeared to be easier to operate, and has the great advantage of providing several hundreds of ignitions per minute from which to collect the data required, whereas a test apparatus usually allows of only a few ignitions being taken per hour.

One outstanding development in apparatus for ignition measurements has been the R.A.E. Spontaneous Ignition Temperature Apparatus (Foord, Symposium [21*c*, 1932]), which is described elsewhere by W. Helmore ('Spontaneous Ignition Temperatures: Determination and Significance', p. 2970). This apparatus consists of a bomb filled with air at atmospheric pressure; an injection of fuel oil can be given with a pump and injector. The temperature of the air can be increased at will, and at each temperature the time lag of ignition can be registered on a paper tape. It was shown that different fuels had different temperature-lag curves, especially the lowest temperatures of ignition being different, whilst the lags at temperatures around 600° C. did not vary much. Besides, these lags are from 10 to 100 times longer than those in an engine. Le Mesurier and Stansfield (Symposium [21*d*, 1932]) found that the test gave a good indication for starting properties, but not so for delay angle under running conditions.

Engine tests have been made for two purposes: firstly, to find the lowest temperature or compression ratio at which the engine would fire on the fuel tested; secondly, to find the lag of the fuel under test under running conditions.

(*c*) Starting Tests.

Starting tests have been described by Le Mesurier and Stansfield [10, 1931] and by Pope and Murdock [16, 1932]. The former elaborated their method (Symposium [21*d*, 1932]), which consists in motoring an engine at a constant speed and heating up the air as well as the cooling water to the same temperature; an injection of fuel is given which will usually fire immediately. The temperatures of air and water are then reduced 10° C. and another test is made; the temperatures are lowered until a misfire occurs, after which final adjustments of the temperatures follow. Each fuel thus provides a limiting starting temperature.

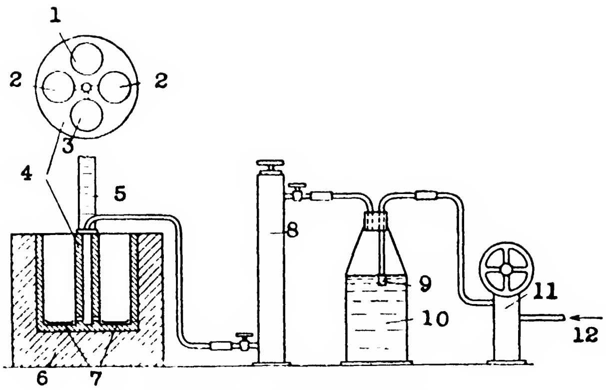


FIG. 6. Jentzsch ignition tester

1. Thermometer pocket
2. Auxiliary chamber
3. Admission chamber
4. Ignition crucible
5. Thermometer
6. Furnace
7. Vaporization dish
8. Drier
9. Jet
10. Bubble counter
11. Adjusting valve
12. Oxygen supply

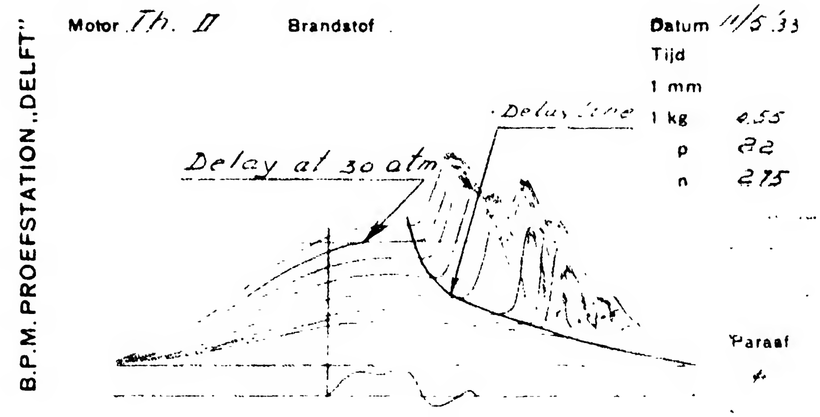


FIG. 7. Indicator diagram from the Thomassen engine

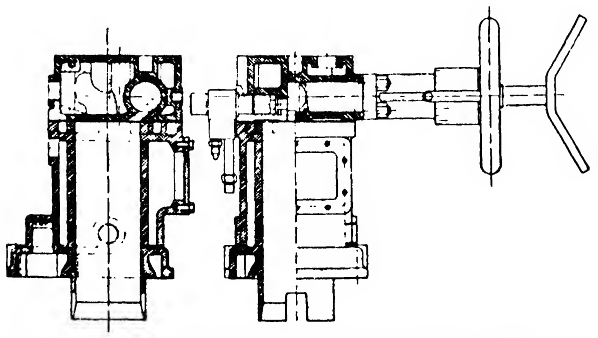


FIG. 8. Cylinder and head of the converted C.F.R. engine

Figs. 6–8 are reproduced by permission from 'J. Inst. Petroleum Technologists', vol. 18, 1932

Pope and Murdock utilized an adapted C.F.R. petrol-testing engine with variable compression, which they equipped with an injection system and a piston with a cup-shaped indentation. Their procedure was to motor the engine at 600 r.p.m. with fixed air and water temperatures and to inject fuel during 3 sec. If the fuel fires, the compression ratio is decreased step by step until no firing within 3 sec. is obtained. The compression ratio at which this occurs is called the 'Critical Compression Ratio' (C.C.R.). The C.C.R. was found to vary between 7 and 15 on the engine described; it was found later (Becker and Stacey [17*a*, 1933]) that the rate of fuel feed, the number of injections given, and the air temperature greatly influence results, so that the method must be strictly specified. It has been in use unofficially in the U.S.A. for some time now; since 1933–4 another modification has been introduced into the engine, which will be described below.

(*d*) Running Tests.

Boerlage and Broeze proposed [1, 1931] to rate fuels on ignition quality in terms of ignition lag under normalized conditions, after having found that ignition-lag measurements in different engines showed a sufficient correlation. The engine used was a low-speed engine on which diagrams were taken of the injector valve lift and of the pressure. Fig. 7 shows the two diagrams taken on a single paper. In order to obtain results independent of engine characteristics they proposed to use reference fuels, such as has been the practice in petrol knock rating. Cetene and mesitylene were at first suggested, but later (Broeze, Symposium [21*a*, 1932]) 1-methyl-naphthalene was substituted for mesitylene on the score of cost. A practically perfect correlation was found between these cetene figures and octane figures determined in a petrol engine. These tests were made originally on a slow-running direct injection Thomassen engine 40 h.p., 250 rev.; later on it was tried to apply the method of lag measurements to the Diesel conversion of the C.F.R. engine, but this failed at first owing to the fact that combustion in the original conversion was unsatisfactory; in collaboration with the builders of the engine, the Waukesha Motor Company, a new combustion chamber arrangement was designed employing a turbulence chamber with variable compression ratio (Fig. 8). Instead of the diagrams, which had to be measured out, it was proposed to make use of a modification of the well-known 'bouncing pin' and an electrical measuring circuit so arranged that the amounts of current passing during the ignition lag could be registered. The advantage would be that every cycle of the engine contributed to the measurement, which therefore would be the average of a high number of actual ignitions (World Petroleum Congress [17*b*, 1933]). Work on this development is in progress, notably in the U.S.A.

An entirely different kind of running test was proposed by Dumanois [3, 1933], who made use of the similarity between self-ignition in the Diesel engine and detonation in the petrol engine. The fuel was mixed up to a certain percentage in a given petrol with a known octane number, and the variation in octane number was noted. The more the octane number decreased, the higher the ignition quality of the fuel. For a certain number of fuels this test correlated well with measurements on Diesel engines.

(*e*) Reference Fuels.

Any attempt to find a suitable rating for ignition quality depends, of course, on the degree of correlation found between results of tests on varying engine types; a good survey of work done is found in the *Proceedings of the World Petroleum Congress* [17].

The proposal to use reference fuels which would enable measurements made on different engines and in different ways to be correlated was accepted at that Congress [17]. Cetene and 1-methyl-naphthalene were agreed upon to serve tentatively for this purpose. The formulae and further specifications of these substances are given in Table V.

TABLE V

Cetene:		
A.S.T.M. dist.		
I.B.P.	$>265°$ C.	
F.B.P.	$<295°$ C.	
Dist. between 270 and 280° C.	$>90\%$	
Melting-point	3·8–4·2° C.	
Bromine number McIlhiney	68 72	
s.g. 20/4	0·780–0·782	
n_D^{20}	1·4400	
Mol. refr. (D)	1·4420	
1-Methyl-naphthalene:		
A.S.T.M.: I.B.P.	230° C.	90% within 1·5° C.
F.B.P.	238° C.	98% below 238° C.
Melting-point picrate	137–141° C.	
n_D^{20}	1·6165–1·6170	
d_4^{20}	1·0200–1·0190	

Cetene Number. The cetene number of a fuel is the percentage by volume of cetene in the cetene and 1-methyl-naphthalene blend that matches the fuel in question in ignition quality (lag, critical compression ratio, or otherwise). In view of the little general experience obtained, no standardized method of determining cetene numbers has been agreed upon as yet, so that figures obtained with different methods must still be treated carefully; in particular it appears that cetene numbers obtained by the C.C.R. or a similar method are somewhat higher than those obtained on a lag basis, the latter agreeing well, however, between one engine and another.

It has been found that cetene numbers, when expressed in weight instead of volume percentage, were additive (Boerlage and Broeze [2, 1932]), so that for fuel blends (equally expressed in weight proportions) the cetene numbers showed a linear relationship. This may serve as a rule when blending fuels; it is also a point for reconsidering the weight basis. Measuring fuel by volume is, moreover, less attractive for viscous and dark-coloured Diesel fuels than measuring by weight.

Cetane Number. The American Society for Testing Materials issued a classification of Diesel Fuel Oils in June 1934 (A.S.T.M. Standards on Petroleum Products, Committee D. 2, 1936, p. 34) and the Cetane Number is given as the measure of ignition quality. It is stated that it has been found that more reliable results may be possible when using cetane rather than cetene. For this reason the classification substitutes the Cetane Number, which is determined and expressed in the same manner as the Cetene Number, namely, as the percentage of cetane in a blend of cetane and 1-methyl-naphthalene.

(*f*) Ignition Indices.

Almost every investigator working on ignition quality has at some time endeavoured to find a simpler test for this quality than the engine test. Apart from the S.I.T. tests and the test of Dumanois, which are actual ignition tests under conditions other than those in the C.I. engine, use has been made of the tendency to soot (T.T.S.), after it was shown that kerosines of certain crudes had a T.T.S. more or less related to the cetene number of corresponding gas oils

(Floor, unpublished tests, 1932, Bataafsche Petroleum Mij.). This test shows indeed a fair correlation for commercial fuels, but fails for synthetic products and doped products.

Of entirely different character are *indices* which attempt to correlate the ignition quality (a function mainly of the chemical composition) to some physical or chemical characteristic which is also a function of the chemical composition. All such indices are based on the purely accidental fact that for natural petroleum hydrocarbons the external characteristics bear a certain relationship to the chemical composition. Strongly branched hydrocarbons or compounds containing oxygen or other elements besides C or H drop out of this picture entirely; the indices are, therefore, of somewhat restricted use; the correlation with engine tests is, according to the authors' experience, moderately good for most of the indices proposed, of which no single one in particular excels. Comparison of these different indices with the Cetane Number rating has recently been made by Schweitzer and Hetzel [19*a*, 1936]; using 19 different fuels, none of the empirical ratings tried —Aniline Point, Diesel Index, Viscosity Gravity Index, Viscosity Slope Index—were found to be an entirely satisfactory substitute for actual engine-testing. The following table summarizes the better-known indices proposed.

TABLE VI

Indices for Ignition Quality

1. W. H. BUTLER. *Ignition Index.* (*J.S.A.E.*, July 1931, *Diesel Power*, Sept. 1931.)

$$x = (1 - \text{s.g.}/100^\circ\ \text{F.})\ \frac{\text{s.g.}/100^\circ\ \text{F.}}{100 \times \text{dispersion}/100^\circ\ \text{F.}} \times \text{average boiling-point in } ^\circ\text{F.} = 50\%\ \text{A.S.T.M. dist. point.}$$

100 is ideal.
Quality decreases with x.
Range of normal fuels 35–60.

2. G. D. BOERLAGE and J. J. BROEZE. *Ignition Index.* (*J.S.A.E.*, July 1932, p. 283.)

$$I = \text{sp. gr.} - 0{\cdot}00075\ (50\%\ \text{A.S.T.M. dist. pt. (in } ^\circ\text{C.)} - 250^\circ\ \text{C.)}.$$

The lower the value of I, the higher the ignition quality. Range of normal fuels 0·82–0·90.

3. L. J. LE MESURIER and R. STANSFIELD. *Aniline Point.* (*Inst. Mar. Eng.*, April 1934.)

Temperature at which equal volumes of aniline and oil are just miscible.
Ignition quality increases with aniline point. Range of normal fuels 40–75° C.

4. A. E. BECKER and H. G. M. FISCHER. *Diesel Index.* (*J.S.A.E.*, Oct. 1934, p. 376.)

$$\text{D.I.} = \frac{\text{Aniline Point } (^\circ\text{F.}) \times \text{A.P.I. gravity}}{100}.$$

Ignition quality increases with D.I.; Range of normal fuels 30-80.

5. G. C. MOORE and C. R. KAYE. *Viscosity-Gravity Index.* (*Proc. 15th Ann. Meeting A.P.I.*, Nov. 1934.)

A = viscosity-gravity constant
G = specific gravity
KV = kinematic viscosity in millistokes/100° F.

Ignition quality decreases with increasing A.
Range of viscosity-gravity constant A 0·93–0·81 for normal fuel.

$$G = 1{\cdot}082A - 0{\cdot}0887 + (0{\cdot}776 - 0{\cdot}72A)[\log\log(KV - 4)].$$

(*g*) Dopes for improving Ignition Quality.

It has been proposed at different times to improve the ignition quality of Diesel fuels by the addition of some active substance, e.g. nitro-compounds such as ethyl nitrate (Sims [20, 1928]) and organic peroxides; the matter is still in the research stage (vide *Combustion Research in C.I. Engines*, chapter ii).

REFERENCES

1. BOERLAGE, G. D., and BROEZE, J. J. *Engin.*, 1931.
2. ——— *J.S.A.E.*, 1932.
3. DUMANOIS, P. *Comptes Rendus des séances de l'Académie des sciences à Paris*, 3 April 1933, p. 1003.
4. ERK. *Der Vogel-Ossag Viscosimeter, Forschungsarb. 288 VDI.* Berlin, 1927.
5. EVERETT, P. N. *Diesel Fuel.* The Anglo-Persian Oil Co., London, 1934.
6. HAWKES, C. J. *Engin.* **110**, ii, p. 749, 1920.
7. HERSEY, M. D. *N.A.C.A. Tech. Notes*, 315, 1929.
8. HOLDE, D. *Kohlenwasserstofföle und Fette.* Berlin, Springer, 1933 (7th Edition).
9. HOLM, H. *Z. angew. Chemie.* **26**, 1913.
10. LE MESURIER, L. J., and STANSFIELD, R. *J.I.P.T.*, 1931, p. 387.
11. ——— *North-East Coast Inst. Engn.* and *Shipb.*, 1932.
12. LUNGE-BERL. *Chemisch-technische Untersuchungsmethoden*, **1**, 447. Springer, Berlin, 1921.
13. MCILHINEY. *Z. angew. Chemie*, **33**, 1920.
14. MOORE, H. *Fuel Oil for Heavy Oil Engines.* World Power Conference, 1928.
15. —— *Liquid Fuel.* Technical Press, London, 1935.
16. POPE, A. W., and MURDOCK, R. *J.S.A.E.*, Feb. 1932.
17. *Proceedings World Petroleum Congress, 1933.*
    (*a*) BECKER, A. E., and STACEY, H. R. Measurement of Ignition Qualities of Diesel Fuels.
    (*b*) BOERLAGE, G. D., and BROEZE, J. J. Knock-rating for High-Speed C.I. Engine Fuels.
    (*c*) POPE, A. W. The Measurement of Injection-Engine Fuel Ignition Properties.
    (*d*) STANSFIELD, R. The Ignition Quality of Fuels for C.I. Engines and Proposals for Its Determination.
18. SASS, F. *Kompressorlose Dieselmaschinen.* Springer, Berlin, 1929.
19. —— *Beitrag zur Normung der Diesel-Treiböle. Werft, Reederei, Hafen*, 1 March 1935.
19*a*. SCHWEITZER, P. H., and HETZEL, T. B. *J.S.A.E.* **38** (5), 206 (1936).
20. SIMS, C. J. B.P. 294,129 (1928).
21. Symposium on Spontaneous Ignition Temperatures. *J.I.P.T.* **18**, no. 105, July 1932, p. 553.
22. TAUSZ, J., and SCHULTE, F. *Ueber Zündpunkte und Verbrennungsvorgänge im Dieselmotor.* W. Knapp, Halle, 1924, p. 9.
23. VLUGTER, WATERMAN, and VAN WESTEN. *J.I.P.T.* 935-50, 1932.
24. WOLLERSAND EHMCKE. *Kruppsche Monatshefte*, **2** (1921).

DIESEL FUEL

By L. J. LE MESURIER, M.I.N.A., M.Inst.P.T.

Anglo-Iranian Oil Company, Ltd.

THE title is intended to include all fuels used in engines in which the fuel is directly injected into the cylinder and atomized prior to ignition and combustion. It does not include fuels for engines fitted with external vaporizers where a vaporized or partly vaporized mixture of air and fuel is drawn into the cylinder during the suction stroke and ignited by means of an electric spark or hot spot. Although such engines may in some cases operate on Diesel fuels, they are more commonly supplied with light-grade fuels approximating to kerosine.

Engines using Diesel fuel are known by various names, such as hot bulb engines, surface ignition engines, compression ignition engines, cold start engines, crude oil engines, Diesel engines, &c. In the hot bulb type air is drawn or pumped into the cylinder and compressed to a moderate pressure of 100–250 lb. per sq. in., and ignition is effected by the fuel spray coming in contact with a heated surface or hot bulb which forms an unjacketed portion of the cylinder head. In the compression ignition or Diesel type, compression is raised to a higher degree, say 400–500 lb. per sq. in., and the temperature reached by the air during compression is sufficient to cause the fuel to ignite. In all such engines the temperature reached by the air is considerably above the self-ignition temperature of the fuel.

Atomization of fuel in the cylinder is brought about by injecting the fuel through an orifice at high velocity and breaking up the fuel into fine droplets which are dispersed throughout the air-space. This effect may be brought about in many different ways, resulting in either coarse or fine atomization and with varying degrees of penetration of the fuel spray throughout the air charge.

The method adopted in the original Diesel engines, and still used to some extent in large slow-running engines, is to employ a cam-operated needle valve which fits in a casing to which a fuel pump delivers a measured quantity of fuel. The valve casing is supplied with injection air maintained under pressure by means of a separate air pump or compressor driven by the engine, and when the needle valve is lifted by a cam at the correct moment, the fuel contained in the casing is blown into the cylinder at very high velocity, with the result that a fine spray is dispersed throughout the combustion chamber between the piston and cylinder head. This type of injection is known as air or blast injection and enables a very fine penetrative spray to be formed, and also provides additional air for combustion through the effect of the injection or blast air which may amount to between 5 and 10% of the swept cylinder volume.

Air-injection valves are arranged with pulverizer plates or other means for ensuring an intimate mixture of the air and fuel leaving the nozzle. These arrangements provide means for modifying the conditions of spray to suit different grades of fuels, and a further adjustment is possible by varying the pressure of blast air.

Air injection is generally found to be suitable for operation over a wide range of fuels on account of the easy means available for varying the spray conditions. On the other hand, it has the disadvantage of the extra complication and expense of a high-compression air compressor which also reduces the mechanical efficiency of the engine on account of the power absorbed by this unit. The cooling effect of the high-pressure injection air issuing from the fuel nozzle also tends to make starting more difficult, particularly when the engine is cold. These disadvantages have been found sufficient to cause the abandonment of this type of fuel injection in practically all modern engines which are operated on the more sensitive, but simpler and more efficient, method known as airless, mechanical, or solid injection.

In airless injection engines the fuel, in a measured quantity, is delivered at high pressure directly into the cylinder through a small orifice. Atomization of the fuel is effected by the high velocity attained in the nozzle orifice, the fuel being torn off into small droplets as it emerges into the combustion chamber. In air-injection engines the blast air pressure may be 700–1,200 lb. per sq. in., depending on the load and type of fuel valve, but in the airless injection system the fuel has to be raised to a much higher pressure in order to secure proper atomization, and pressures ranging from 1,500 to 10,000 lb. per sq. in. are employed.

Many different systems are used for controlling the correct quantity of fuel and its admission in the form of a suitable spray at the correct moment. In most airless injection engines the fuel pump is timed to deliver a measured quantity of fuel at the correct moment to a fuel valve situated in the cylinder head. This valve is usually a spring-loaded needle valve fitted close to the spray orifice and so designed that it opens and closes rapidly, according to the commencement and end of the fuel-pump delivery. In some cases the fuel-injection valve may be mechanically controlled as in an air-injection engine, while in other cases the valve is omitted altogether so that injection takes place through an open nozzle during the pump delivery. The common object in all systems of fuel injection is that the fuel should be broken up into sufficiently fine droplets and that these droplets should be so dispersed throughout the air in the cylinder that they are readily ignited and burnt.

Diesel fuels are generally produced from petroleum crude oil from which light volatile fractions have been extracted by a distillation process, thus leaving a fuel of relatively high flash-point. The nature of different crude oils varies to such a wide extent that no general method of manufacture of Diesel fuel can be applied to all crudes. Some light crude oils produce satisfactory Diesel fuels without the need of any further treatment than the removal of the light volatile material which would otherwise cause a low flash-point. Other crude oils with a large amount of heavy asphaltic material or containing sand or other impurities require to be distilled in order to obtain fractions satisfactory for use in engines.

Substances other than petroleum crude oil may also be used for the production of Diesel fuel, as, for instance, coal-tar and shale distillates, vegetable oils such as palm oil, rapeseed and colza oils, and animal oils and fats.

The general characteristics and properties of Diesel fuels can be divided into those affecting

(1) the handling, storage, and pumping of the fuel until it enters the cylinder, and

(2) the ignition and combustion of the fuel after injection.

It is usual to include a number of these properties in Diesel fuel specifications, although it is impossible to define with any exactitude the merit of a Diesel fuel by reference to specification characteristics.

Conditions (1) are chiefly affected by the following qualities:

(*a*) Flash-point.
(*b*) Specific gravity.
(*c*) Viscosity and set-point.
(*d*) Impurities.

Conditions (2) are dependent upon the following:

(*a*) Calorific value.
(*b*) Distillation range.
(*c*) Chemical composition.
(*d*) Carbon residue and asphaltic matter.

Flash-point.

The flash-point of all Diesel fuels is generally arranged to be not less than 150° F. This requirement is introduced solely as a safeguard against fire risks when handling and storing the fuel. The figure of 150° F. is commonly specified by government departments, insurance companies, and others interested in the safety of the fuel. Flash-point is otherwise of no practical importance and has no effect either on the ignition or combustion of the fuel in the engine.

Specific Gravity.

Other conditions being equal, the output of an engine is governed by the total input of heat available from the weight of fuel burnt and its calorific value.

In general, the lower the specific gravity of the fuel the higher will be its calorific value, and consequently a greater power output is obtainable from a given weight of low specific gravity fuel. Although heat units per unit weight increase as specific gravity decreases, the heat available per unit volume decreases, so that when changing from high to low specific gravity fuel the fuel-pump control must be set to give a greater pump-volume delivery, although the weight of fuel pumped will be slightly less.

As an example of the relation between specific gravity and calorific value, the following figures are extracted from a table published by the Institute of Petroleum Technologists on 'Measurement of Oil in Bulk' by Mr. J. McConnell Sanders:

Sp. gr. 15·4° C.	*Calories per kilo.*	*Calories per litre.*
0·704	11,769	8,272
0·746	11,421	8,507
0·821	11,083	9,087
0·857	10,841	9,279
0·934	10,387	9,690
0·954	10,358	9,870

Generally speaking, the calories per kilo decrease with increasing specific gravity, whilst the calories per litre increase. The specific gravity of fuel has no direct influence on its behaviour in the engine, but it is a useful indication of the origin of the type of fuel and affords a simple means by which the purchaser can check uniformity in supplies of fuel.

Viscosity and Set-point.

The property of viscosity is of great importance as it affects the use of the fuel right from the storage tank up to the engine-fuel injection valve and also influences the type of spray produced in the cylinder. It is essential that the fuel should flow freely to the fuel-injection pump so that the volumetric efficiency of the pump is not impaired, and so that no air is drawn into the fuel system due to conditions arising in the pump suction which may allow the fuel to come under less than atmospheric pressure. Thus, when fuels of high viscosity are used it becomes advisable to fit a pipe system of liberal dimensions and to provide filters, pipe bends, and pipe system of such design that the fuel remains at least under atmospheric pressure up to the time it enters the fuel pump. Alternatively, where fuels having a high viscosity at atmospheric temperature are used, it is possible by heating the fuel to reduce the viscosity to a suitable degree so that it flows freely to the pump.

Ordinary commercial Diesel fuels have viscosities sufficiently low to meet the conditions obtaining in engine installations of normal design where the fuel system is so arranged that there is always a slight positive head on the fuel-suction line. The viscosity of such fuels usually averages from about 35 sec. to 100 sec. Redwood No. 1 at 100° F. The appropriate viscosity of Diesel fuels varies to some extent according to the type of engine for which the fuel is required. Small engines having small fuel pumps and pipe systems naturally require fuels of lower viscosity than slow-running engines of large dimensions. The Technical Committee 'C' of the A.S.T.M., Committee D. 2, have prepared the following table of viscosities which is embodied in their classification of Diesel fuels.

Grade of Diesel fuel	*Viscosity sec.*		
	Saybolt Universal at 122° F.		*Saybolt Furol at 100° F.*
	Min.	*Max.*	*Max.*
1-D. A distillate oil for use in engines requiring a low viscosity fuel . . .	32	50	..
3-D. A distillate oil for use in engines requiring a medium low viscosity fuel . .	32	70	..
4-D. An oil for use in engines requiring a medium low viscosity fuel . . .	..	500	..
5-D. An oil for use in engines permitting a medium high viscosity fuel . . .	..	..	100
6-D. An oil for use in engines of special design for high viscosity fuels and after engine manufacturers' recommendations only . .	..	..	300

'Grade 1-D is recommended for mechanical (solid) injection engines of the high-speed type; in general, for engine speeds over 1,000 r.p.m.

'Grade 3-D is recommended for mechanical (solid) injection engines of the medium-speed type; in general, for engine speeds from 360 to 1,000 r.p.m.

'Grade 4-D is recommended for air-injection engines, both two- and four-stroke cycle types, with speeds not over 400 r.p.m. Grade 4-D can be used for mechanical (solid) injection engines with cylinder diameters over 16 in. and speed under 240 r.p.m., but approved heating equipment furnished by the engine manufacturer is recommended.

'Grade 5-D is recommended for air-injection engines of the slow-speed type; speed under 240 r.p.m. Manufacturers should be consulted for approved heating equipment.

'Grade 6-D is not regularly used for Diesel engines and is not recommended unless tested and approved by the engine manufacturer.'

The conversion of Saybolt to Redwood No. 1 scale is as follows:

Saybolt Universal	*Redwood I*
32 seconds	29 seconds
50 "	45 "
70 "	62 "

Saybolt furol	*Redwood I*
100 seconds	840 seconds
300 "	2,540 "

Fuels used in engines of small dimensions such as high-speed engines for road vehicles, tractors, generating sets, &c., have usually a viscosity of less than 40 sec. Redwood No. 1 at 100° F., this being necessary in order to deal with the extremely small fuel pumps, pipes, and fittings in the fuel system. On the other hand, it is not an advantage to have fuel of too low viscosity, approximating, for instance, to kerosine, as with such fuel difficulty may be experienced in maintaining pump plungers and valves in good condition and also in avoiding an undue amount of fuel leakage from these parts.

So far as sprayer action is concerned, the average size of droplets produced from a fuel-spray valve varies with the viscosity of the fuel, a fuel of high viscosity giving rise to larger-sized droplets than a fuel of low viscosity. The larger the droplet the greater will be the degree of penetration, and the longer the time necessary in which to effect complete combustion. Consequently, in engines of small dimensions the fuel spray obtained with the more viscous fuels is liable to reach the walls of the combustion chamber before combustion is completed, an effect which becomes more pronounced as engine speed is increased due to the shorter time available for combustion. Apart, therefore, from the question of the effect of viscosity in the fuel pump and fuel system, consideration must also be given to the results on the fuel spray.

Viscosity does not appear to affect the ignition characteristics of fuels, as experiments have shown that the 'delay angle' or period which elapses before combustion commences after the fuel has been injected does not vary appreciably according to whether the droplets are of large or small dimensions.

Set-point, or pour-point, of Diesel fuels are characteristics which become important when the fuel has to be used under low temperature conditions. The tests usually employed are either the A.S.T.M. Pour-point Test or the I.P.T. Setting Point Test. So far as the operation of engines on fuels is concerned, it is only necessary that these characteristics should be taken into account so that under all conditions of operation it is possible to ensure that the fuel is readily capable of being pumped.

Impurities.

All Diesel fuels are normally found to contain small quantities of water and also of solid material which may be partly or wholly incombustible. Incombustible material, apart from the water, is termed the 'ash' content and is usually very small in quantity, being of the order of 0·05% or less in most commercial Diesel fuels. Although this quantity is small, it is very important that the ash content should be the least possible, as portions of any incombustible material must inevitably reach the cylinder liner walls, mix with the lubricating oil, and be conducive of increased cylinder liner wear. In addition, it also tends to reduce the life of piston rings and exhaust valves.

Water and other impurities usually collect in the fuel during transport and storage, as, for instance, through rust and scale in storage tanks and pipes, and also through atmospheric contamination from dust, sand, &c. Water and adventitious matter lead to difficulties in fuel filters, fuel pumps, and injection valves, apart from any subsequent troubles caused in the cylinder. Every possible precaution should be taken in storage and transport to avoid contamination, which is probably responsible for the majority of troubles that are attributable to the fuel used in oil engines. In most large oil-engine installations, such as those fitted in motor ships and in land installations for industrial purposes, it is customary to install centrifuge separators or else filtering apparatus of special type to ensure that as far as possible all contamination occurring during the transport and storage of the fuel is removed immediately before the fuel reaches the engine.

Calorific Value.

In order to measure the efficiency of an oil engine it is necessary to know the actual number of heat units supplied in a given weight of fuel, or, in other words, the calorific value of the fuel. In all engine tests, therefore, particulars of the fuel used should include the calorific value.

A distinction must be made in this connexion between gross and net calorific value. The gross calorific value represents the total quantity of heat in a given weight of fuel assuming that all the combustible components, which are usually hydrogen, carbon, and sulphur, yield their full heat value. As, however, the hydrogen component is converted into steam which in the case of an engine leaves without giving up its latent heat, it is necessary to subtract the latent heat of this portion in order to arrive at the actual net useful heat input of the fuel used. The net calorific value of the fuel is used to indicate the heat content of the fuel after subtracting the latent heat of the steam formed from the hydrogen content. It is conventional amongst the leading scientific societies to base engine thermal efficiency on the gross calorific value of the fuel.

The gross calorific value of any fuel may be obtained approximately by calculation provided its chemical composition is known. In the case of a fuel containing carbon, hydrogen, oxygen, and sulphur, the gross calorific value is as follows:

$$\text{calories per g.} = \frac{C\,8{,}137 + (H - O/8)34{,}500 + S\,2{,}500}{100}$$

$$\text{B.Th.U. per lb.} = \frac{C \times 14{,}600 + (H - O/8)62{,}500 + S\,4{,}500}{100},$$

where C, O, H, and S represent the percentages of carbon, oxygen, hydrogen, and sulphur in the fuel.

Experimental determination of calorific value is made in a bomb calorimeter, from which the gross calorific value is obtained. The deduction from the gross calorific value to obtain the net calorific value is made by deducting approximately 600 calories per gramme of water formed during combustion, or 54 calories for each 1% of hydrogen in the fuel, thus:

Net calorific value = gross calorific value − 54H, where

H equals the percentage of hydrogen in the fuel. The conversion of calories to British Thermal Units is as follows:

$$1 \text{ calorie} = 1{\cdot}8 \text{ British thermal units},$$

$$1 \text{ British thermal unit} = \frac{5}{9} \text{ calories}.$$

Distillation Range.

While distillation range or volatility is an important factor in fuels for engines of the vaporizer type with an external carburettor, it is relatively of little value in the case of Diesel fuel. The fuel in a Diesel engine is injected in the form of liquid fuel droplets and combustion commences in such a short time after injection that it is impossible under the conditions of pressure existing in the cylinder for any appreciable quantity of the fuel droplets to vaporize before combustion commences. Nevertheless, it is considered by some investigators that gaseous mixtures are formed by evaporation from the drop surfaces in sufficient quantity to affect the combustion process.

Reference may be made in this connexion to the results obtained by C. B. Dicksee [1, 1932], and also to the experimental investigations made by Messrs. Rothrock and Waldron [2, 1932], in which photographs of fuel sprays in heated air are illustrated, these photographs being obtained under conditions approximating to those occurring in an engine.

Distillation tests on Diesel fuels usually show an initial boiling-point varying between 175° C. and 225° C. The final boiling-point may be indeterminate, as when the temperature of distillation is raised above about 350° C. the fuel may commence to crack. The percentage of distillate at intermediate temperatures may vary widely without, however, showing any practical effect on engine performance, and as such fractional distillation results are unimportant it is usual to limit a distillation test to obtaining the total quantity of distillate at a temperature just below the cracking temperature. At 350° C., for instance, the total distillate obtained from average Diesel fuels will vary between about 95 and 25%, and such a test merely serves to indicate broadly whether the fuel is of a light or heavy grade.

Chemical Composition.

All Diesel fuels produced from petroleum fuel consist chiefly of carbon, hydrogen, and a small percentage of sulphur, depending on the source of the crude. In addition, there may be slight traces of nitrogen and oxygen. The hydrocarbons are combined in the fuel in various proportions, and may be divided into three main groups—paraffins, naphthenes, aromatics. It is found that the crude oil in which any particular one of the above-mentioned groups predominate will yield products generally conforming to that particular group; thus Diesel fuel may tend to be paraffinic, naphthenic, or aromatic in nature, according to the origin of the crude.

The approximate percentages of carbon and hydrogen in petroleum Diesel fuels are as follows:

Carbon	max. 88%
,, ...	min. 85%
Hydrogen . . .	max. 14%
,, ...	min. 11%

In general, the higher the hydrogen value the greater will be the calorific value of the fuel, and also the more nearly it will approach to the paraffinic type which, for reasons of good ignition qualities, is generally preferred as a Diesel fuel. All Diesel fuels originating from coal-tar products are chiefly of an aromatic nature and, unless specially treated to reduce the aromatic contents, may have as low as 6% hydrogen and a net calorific value of 16,500 B.Th.U. as against 18,500 B.Th.U. in petroleum-produced fuel. The self-ignition temperature of aromatic fuels is relatively high, resulting in poor ignition qualities on account of the long 'delay' between the moment of injection and ignition. It is, however, possible by means of special treatment of coal-tar products to produce fuels capable of satisfactory operation in Diesel engines.

The ignition quality of fuels and methods of testing the relative qualities of different fuels is dealt with in the article on light Diesel fuels.

With regard to Diesel fuels produced from other sources than petroleum crude, the fuel obtained by distillation from bituminous shales is in many respects similar to that obtained from a paraffinic type petroleum crude. The fuel has a large hydrogen content and high calorific value and is suitable for engine purposes.

Animal and vegetable oils are occasionally used as Diesel fuels. The composition includes, besides carbon and hydrogen, a considerable proportion of oxygen and nitrogen which reduces the net calorific value to about 16,000 B.Th.U. or less.

The following analyses of vegetable oils are given in an article on 'The Employment of Vegetable Oils' by Monsieur Gautier in *Le Génie Civil* of 17 March 1934.

	Sp. gr.	*Set-pt.*	*Flash-pt.*	*Cal. value calories per g.*		*Composition*			
				Gross	*Net*	C	H	O	*Water*
Arachis .	0·910	+5	233	9,660	8,927	75	12	13	0
Palm oil .	0·900	33	105	9,400	8,752	74	12	13	1·45
Karité .	0·915	34	112	9,640	9,017	77	11·5	11	0·10
Cotton seed	0·958	−8	175	9,165	8,557	73·5	11	15	0·01

Arachis and karité are oils obtained from ground-nuts, the plants being chiefly grown on the west coast of Africa and in the Dutch East Indies. Karité is the local name of a plant which is chiefly grown for the production of margarine or shea butter.

The high set-point of these oils may require preheating of the fuel before reaching the engine, but in other respects the engine performance is practically normal, although the specific fuel consumption is naturally higher than for petroleum or shale oils on account of the lower net calorific value.

Carbon Residue and Asphaltic Matter.

Diesel fuels vary considerably in their carbon-forming tendencies, as shown by observation of the internal condition of an engine after a period of running. Carbon may commence to form on the fuel-injection valve flameplate or nozzle, and the interference with spray formation may rapidly lead to a fall-off in output and a smoky exhaust. In some cases carbon may be formed irrespective of the type of fuel used due to the effect of a leaky fuel valve, faulty spraying, or overloading of the engine. Mechanical defects in the engine may also be responsible for the formation of carbon due, for instance, to insufficient cooling of the fuel-valve nozzle, over-lubrication of the piston and cylinder surfaces, or lack of air caused through an obstruction of the air inlet or exhaust systems.

Various tests have been devised with a view to determining the carbon-forming tendencies of fuels. In general, it is considered that a fuel containing asphaltic material as determined by the hard asphalt test will be more difficult to burn completely than a fuel free from this constituent, with the result that carbon is more likely to be formed. The test for hard asphalt is carried out by dissolving the fuel with a light petroleum spirit and determining the percentage of insoluble material which can be removed by filtration. The technique of the test as carried out in England, U.S.A., and Germany is, in principle, the same but the reagent used is different, and results may differ appreciably according to the exact method employed.

In general, however, all light Diesel fuels suitable for high-speed engine operation should show little or no hard asphalt whatever test is used. Heavier grades of fuel used in large marine or land engines have been found to operate satisfactorily with hard asphalt contents up to as much as 10%, but, in general, average commercial Diesel fuels show asphalt contents of the order of not more than 2%. It should be noted that asphalt is a carbonaceous material which is completely combustible and, provided the engine conditions are suitable and there is a sufficient time available for complete combustion, all this material is capable of being completely burnt.

Other tests which are sometimes used as a possible indication of carbon-forming tendencies are the carbon residue tests, such as the Conradson or Ramsbottom tests, in which a quantity of fuel is heated in a closed vessel until all volatile matter is driven off, leaving a coke-like residue. In this test cracking of the fuel takes place, and as it is carried out in a closed vessel no oxygen is present, and consequently combustion such as occurs in an engine cannot take place. Observations of fuels in regard to carbon-forming tendencies appear generally to correlate more nearly with the hard asphalt content than the Conradson or coke residue.

Diesel Fuel Specifications.

It is not possible to make a general specification to cover fuels suitable for all types of engines, but a rough indication of general suitability can be arrived at by specifying certain chemical and physical properties and their limiting proportions as found appropriate for different types of engines.

TABLE I

	High-speed Diesel fuel
Purpose	For engines used for automotive and allied purposes in which the speed is 800 r.p.m. or over and where the operating conditions demand a high standard of performance.
Flash-point (closed)	Min. 150° F.
Hard asphalt content	Max. 0·1%
Ash content	„ 0·01%
Viscosity (Redwood No. 1) at 100° F.	„ 45 secs.
Water content	„ 0·1%
Pour-point*	„ 20° F.
Conradson carbon	„ 0·2%
Sulphur content	„ 1·5%
Distillation--vol. to 350° C.	Min. 85%
Aniline point†	„ 60° C.
Gross calorific value	„ 19,000 B.Th. U. per lb.

* This limit is intended for temperate climates only. In any case, the purchaser shall satisfy himself that his whole equipment is capable of dealing with the oil at the lowest temperature to which the oil will be exposed.

† Tentative test for ignition quality (for fuel of petroleum origin only), pending the development of an engine test.

The B.S.I., in co-operation with Government Departments and scientific and industrial organizations, have prepared the specifications given in Tables I and II, these specifications taking the place of a set of four specifications previously published by the British Engineering Standards Association in 1924.

TABLE II

	Marine and industrial Diesel fuel	*Heavy Diesel fuel.*
Purpose	For engines where the speed does not exceed about 800 r.p.m. e.g. industrial units and main and auxiliary machinery for marine purposes	For large engines where the speed does not exceed 250 r.p.m. and where means can, if necessary, be provided for heating and cleaning the fuel, e.g. large engines for stationary and marine installations where oil engines for auxiliary purposes are not required to use the same fuel as in the main engines.
Flash-point (closed)	Min. 150° F.	Min. 150° F.
Hard asphalt	Max. 2·0%	Max. 4·0%
Ash content	„ 0·03%	„ 0·10%
Viscosity (Redwood No. 1) at 100° F.	„ 60 sec.*	„ 750 sec.
Water content	„ 0·5%	„ 1·0%
Pour-point	„ 30° F.†	(It is considered undesirable to specify limits to the pour-point, but the purchaser should satisfy himself that his whole equipment is capable of dealing with the oil at the lowest temperature to which the oil will be exposed. Where necessary, a definite limit may be agreed between the purchaser and the supplier.)
Conradson carbon	Max. 3·0%	Max. 8·0%
Sulphur content	„ 2·0%	..
Aniline point‡	Min. 45° C.	..
Gross calorific value, B.Th.U. per lb.	„ 18,750	Min. 18,250.

* The maximum viscosity permitted under this specification shall be increased to 100 sec. Redwood No. 1 at 100° F. whenever the Conradson carbon does not exceed 2% and the hard asphalt does not exceed 1·5%.

† This limit is intended for temperate climates only. In any case, the purchaser shall satisfy himself that his whole equipment is capable of dealing with the oil at the lowest temperature to which the oil will be exposed.

‡ Tentative test for ignition quality (for fuel of petroleum origin only), pending the development of an engine test.

Various engine builders have their own fuel specifications in which particulars are given of the properties they consider of importance when selecting fuels for their types of engine.

The following general specification of Diesel fuels is given by Mr. Schenker [3], Chief Engineer of Sulzer Bros., Winterthur:

		For use in Diesel engines	
	Approximate limits (*1*)	*To be specified* (*2*)	*Admissible* (*3*)
Specific gravity at 20° C.	0·79 to 0·97	0·8 to 0·97	0·8 to 0·97
Flash-point (Open Test)	0° to 170° C.	over 65° C.	20° C. and over
Viscosity at 50° C. Engler degrees	1·5 to 200	below 5	up to 80
Viscosity Redwood 1 at 120° F. sec.	45 to 6,000	below 150	up to 2,400
Net calorific value (undried sample), Calories per kilogram	8,500 to 10,200	10,000	9,600 and over
Ash content, % by wt.	0 to 0·5	below 0·05	not over 0·1
Sulphur content, % by wt.	0 to 5	not over 2	not over 3
Residue at 400° C. (pitch) % by wt.	0 to 25	not over 5	not over 15
Water content, % by wt.	0 to 10	not over 1	not over 5

Messrs. Harland & Wolff, Belfast, give the following specification:

	Small engines	*Large engines*
	(*a*)	(*b*)
Flash-point (closed test) not lower than	150° F.	150° F.
Viscosity at 100° F. (Redwood No. 1) preferably not more than	75 sec.	250 sec.
Ash content not more than	0·01%	0·05%
Hard asphalt not more than	1%	2·0%
Water and sediment not more than	0·5%	1·0%
Coke value not more than	2·0%	3·0%
Gross calorific value preferably not less than B.Th.U. per lb.	19,000	19,000
The oil to remain fluid down to	20° F.	35° F.

Any Diesel fuel specification must necessarily have very wide limits if it is intended to include all suitable Diesel fuels. Within these limits it is, however, always possible to find some fuels which in such respects as ignition quality may fail to give satisfactory engine performance. Further investigation is needed in order to interpret existing physical and chemical tests in terms of engine performance and also in order to develop a reliable test of ignition quality. For the present, the suitability of Diesel fuel for engine purposes can only be obtained with reliability by actual test in an engine.

REFERENCES

1. DICKSEE, C. B. *Some Problems connected with High Speed Diesel Engine Development.* Institution of Automobile Engineers, March 1932.
2. *N.A.C.A. Report* No. 435, 1932.
3. SCHENKER, W. *Fuel and Lubricating Oils for Diesel Engines.*

SELECTED BIBLIOGRAPHY

BOERLAGE, G. D., and BROESE, J. J. The Ignition Quality of Fuels in Compression Ignition Engines. *Engineering*, **132**, Nov. 1931.

LE MESURIER, L. J., and STANSFIELD, R. Fuel Testing in Slow and High Speed Diesel Engines. *J.I.P.T.* **17**, 1931.

—— —— Combustion in Heavy Oil Engines. *North East Coast Institution of Engineers and Shipbuilders*, 1932.

MOORE, HAROLD. *Liquid Fuels.*

Symposium on Spontaneous Ignition Temperatures. *J.I.P.T.* **18**, 1932.

Diesel Oil for the Merchant Marine. World Power Conference 81, Section 9, 1933.

OIL GAS

By LEON J. WILLIEN

Operating Gas Engineer, Byllesby Engineering and Management Corporation, Chicago, Illinois

THE major uses of oil in the manufactured gas industry are for the manufacture of

1. Carburetted Blue Gas.
2. Pacific Coast Oil Gas.

Tables I to IV inclusive show the following by years for the 6-year period from 1929 to 1934. The data pertain only to the United States:

Table I. Manufactured Gas Produced and Purchased for Distribution to Consumers.

Table II. Manufactured and Natural Gas sold to Consumers.

Table III. Manufactured Gases Produced.

Table IV. Fuel Consumed in the Manufacture of Gas.

Carburetted Blue Gas.

For the 16-year period—1919 to 1934—61% of all the gas manufactured in the United States for distribution to consumers was carburetted blue gas manufactured by the Lowe Process. This process was invented in 1872–5 by Prof. T. S. C. Lowe at Norristown, Pa. It is an intermittent process in which blue gas and oil gas are simultaneously produced and mixed in connected pieces of apparatus. The function of the oil gas is to enrich the blue gas. Attempts to enrich blue gas, prior to Lowe's invention, were unsuccessful. Lowe's Process makes the enriching oil gas in a separate chamber that is heated internally by the combustion of producer gas formed in a blue-gas generator.

TABLE I

*Manufactured Gas Produced and Purchased for Distribution to Consumers**

	1934	1933	1932	1931	1930	1929
	Unit: million cubic feet					
Total gas produced	250,909	243,677	261,091	294,223	303,798	308,983
Gas purchased:						
Coke oven gas	92,134	86,977	92,424	109,456	118,464	114,944
Oil refinery gas†	2,541	2,809	1,743	1,473	2,009	2,176
Natural gas	41,122	33,691	27,158	6,428	1,968	1,578
Total gas purchased	135,797	123,477	121,325	117,356	122,441	118,698
Total gas produced and purchased	386,706	367,154	382,416	411,579	426,239	427,681
Per cent. of gas purchased	35·2	33·6	31·7	27·5	28·6	27·6
	Unit: million cubic metres					
Total gas produced	7,106	6,901	7,394	8,332	8,604	8,750
Gas purchased:						
Coke oven gas	2,609	2,463	2,624	3,100	3,355	3,255
Oil refinery gas†	72	76	49	42	57	62
Natural gas	1,167	954	769	182	56	45
Total gas purchased	3,848	3,493	3,442	3,324	3,468	3,362
Total gas produced and purchased	10,954	10,394	10,836	11,656	12,072	12,112

* American Gas Association Statistical Bull. no. 17 (Oct. 1935).

† Does not include quantity used in production of reformed oil refinery gas.

TABLE II

Manufactured and Natural Gas sold to Consumers

	1934	1933	1932	1931	1930	1929
	Unit: million cubic feet					
Manufactured gas*	347,543	334,168	352,175	384,262	396,111	394,539
Natural gas†	960,270	837,741	807,831	879,250	958,590	957,887
Total gas	1,307,723	1,171,909	1,160,006	1,263,512	1,354,701	1,352,426
Per cent. of manufactured gas	26·5	28·6	30·4	30·4	29·2	29·2
Per cent. of natural gas	73·5	71·4	69·6	69·6	70·8	70·8
	Unit: million cubic metres					
Manufactured gas	9,840	9,464	9,974	10,882	11,217	11,174
Natural gas	29,140	25,420	24,514	26,682	29,090	29,067
Total gas	38,980	34,884	34,488	37,564	40,307	40,241

* American Gas Association Statistical Bull. no. 17 (Oct. 1935).

† American Gas Association Statistical Bull. no. 18 (Oct. 1935). These figures do not include natural gas used in field operations and in the manufacture of carbon black, or gas used by distributing companies in the conduct of their gas operations. Companies selling mixed manufactured and natural gas are not included.

TABLE III

*Manufactured Gases produced**

	Unit: million cubic feet					
	1934	*1933*	*1932*	*1931*	*1930*	*1929*
Water gas	156,625	152,957	170,499	190,635	205,856	213,549
Coke oven gas	53,466	51,366	49,267	56,266	50,839	48,814
Retort coal gas	30,016	29,534	32,084	38,043	40,070	41,118
Oil gas	3,176	3,607	4,017	4,287	4,739	4,846
Reformed oil refinery gas	4,781	4,593	4,705	4,478	2,205	646
Reformed natural gas	1,985	947	..	..	..	..
Butane-air gas	859	670	519	514	89	10
Propane gas	..	2	..	..	..	..
Pintsch gas	1	1	..	..	..	..
Total gas produced	250,909	243,677	261,091	294,223	303,798	308,983
	Unit: million cubic metres					
Water gas	4,753	4,642	5,174	5,785	6,247	6,479
Coke oven gas	1,622	1,559	1,495	1,707	1,543	1,481
Retort coal gas	911	896	974	1,154	1,216	1,248
Oil gas	96	110	122	130	144	147
Reformed oil refinery gas	145	139	143	136	67	20
Reformed natural gas	60	29	..	..	..	..
Butane-air gas	24	19	15	15	3	..
Propane gas	..	..	..	..	..	..
Pintsch gas	..	..	..	..	..	..
Total gas produced	7,611	7,394	7,923	8,927	9,220	9,375

* American Gas Association Statistical Bull. no. 17 (Oct. 1935).

TABLE IV

*Fuel consumed in the Manufacture of Gas**

	Units: Coal and Coke, tons of 2,000 lb.; Oil, U.S. gallons					
	1934	*1933*	*1932*	*1931*	*1930*	*1929*
Water gas production (generator fuels):						
Anthracite coal	82,000	46,000	33,000	37,000	84,000	101,000
Bituminous coal	478,000	399,000	463,000	600,000	601,000	614,000
Coke	1,264,000	1,273,000	1,562,000	1,891,000	2,207,000	2,361,000
Coke breeze	26,000	25,000	27,000	20,000	14,000	20,000
Total generator fuel	1,850,000	1,743,000	2,085,000	2,548,000	2,906,000	3,096,000
Boiler fuels:						
Anthracite coal (includes screenings)	104,000	86,000	82,000	98,000	117,000	166,000
Bituminous coal	388,000	337,000	413,000	531,000	637,000	695,000
Coke	90,000	84,000	77,000	104,000	153,000	150,000
Coke breeze	404,000	422,000	460,000	489,000	454,000	423,000
Total solid fuel	986,000	929,000	1,032,000	1,222,000	1,361,000	1,434,000
Oil, 1,000 gal.	11,072	9,726	9,136	16,072	24,578	21,610
Coal and oven gas production:						
Bituminous coal carbonized	7,464,000	7,042,000	7,160,000	8,314,000	8,169,000	8,097,000
Bench and producer fuel	..	..	..	..	..	..
Bituminous coal	16,000	14,000	7,000	15,000	19,000	33,000
Coke	744,000	702,000	715,000	920,000	937,000	921,000
Coke breeze	75,000	70,000	61,000	53,000	9,000	29,000
Total fuels	835,000	786,000	783,000	938,000	965,000	983,000
Oil:						
Carburetting water gas, 1,000 gal.	483,228	479,747	533,216	589,932	628,179	624,179
Making oil gas, „	27,737	31,635	35,211	40,791	45,637	44,977
Total oil, „	510,965	511,382	568,427	630,723	673,816	669,156
Totals:						
Anthracite coal	186,000	132,000	122,000	135,000	201,000	267,000
Bituminous coal	8,349,000	7,792,000	8,043,000	9,460,000	9,426,000	9,439,000
Coke	2,098,000	2,059,000	2,354,000	2,915,000	3,297,000	3,432,000
Coke breeze	505,000	517,000	548,000	562,000	477,000	158,000
Total solid fuel	11,138,000	10,500,000	11,060,000	13,022,000	13,401,000	13,610,000
Total oil, 1,000 gal.	522,037	521,108	577,563	646,795	698,394	690,766
Lb. generator fuel per 1,000 cu. ft. water gas produced	23·6	22·8	24·3	26·7	28·2	29·0
Gallons of carburetting oil per 1,000 cu. ft. water gas produced	3·10	3·14	3·14	3·09	3·05	2·93
Gallons of oil per 1,000 cu. ft. oil gas	8·70	8·75	8·80	8·55	9·60	9·30
Cubic feet of coal gas per ton of coal carbonized	11,200	11,500	11,300	11,300	11,150	11,100

* American Gas Association Statistical Bull. no. 17 (Oct. 1935). Companies formerly distributing manufactured gas but which were distributing natural gas at the beginning of 1934 have been excluded from tabulation for all six years.

Description of Apparatus.

Fig. 1 is a diagrammatic drawing of a three-shell carburetted blue-gas machine equipped with a backrun. This is a type of machine that is in general use to-day. It consists of three brick-lined cylindrical steel shells: the generator, the carburettor, and the superheater. The generator is equipped with a grate for supporting a fuel bed and a fuel-charging door at the top. Below the grate, connexions are provided for introducing air and steam and a gas exit. At the top is a gas-outlet connexion to the top of the carburettor. The carburettor and superheater as shown in the figure are connected at the bottom by a brick-lined gasway and are partly filled with checker brick. At the top of the carburettor there is an oil spray, and at the top of the superheater a stack valve and a gas connexion leading to a washbox through a three-way backrun valve. There is a provision for introducing air into the connexion between the top of the generator and the top of the carburettor.

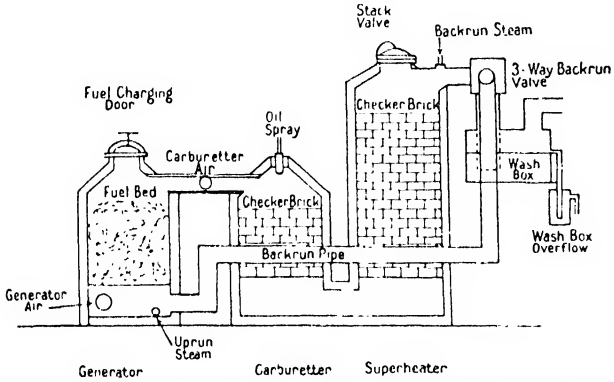


FIG. 1. Diagrammatic sketch of a three-shell carburetted blue-gas machine.

Description of Process.

Coke, anthracite coal, bituminous coal, and oil are the chief raw materials used for making carburetted blue gas. Fig. 2 is a material flow sheet for a carburetted blue-gas plant. The operating procedure is as follows:

Fuel is placed in the generator and heated to incandescence by blowing air through the fuel. The air in passing through the fuel bed forms producer gas. The producer gas passes from the top of the generator into the top of the carburettor. Air is introduced into the connexion between the tops of the generator and the carburettor for the combustion of the producer gas. The hot products of combustion travelling down through the checker brick of the carburettor and up through the superheater heat these parts of the apparatus and pass out through the stack valve at the top of the superheater. This operation is known as a blow. When the proper temperatures are obtained in the fuel bed and the checker brick, the air is shut off and the stack valve closed. Steam is admitted into the bottom of the generator, passes up through the incandescent fuel, reacts chemically with the carbon and forms blue gas which consists mostly of CO and H_2. The blue gas passes from the top of the generator into the top of the carburettor. Oil is introduced into the carburettor through the oil spray at the top. The oil vaporizes, mixes with the blue gas, and passes down through the checker brick in the carburettor and up through the superheater. In their passage through the hot checker brick the oil vapours are cracked into permanent gases. The mixture of blue gas and oil gas is carburetted blue gas. It passes from the top of the superheater through the three-way backrun valve into the washbox. From the washbox it passes to a relief holder. This operation is known as an uprun. When the proper amount of oil has been introduced, the oil and steam are shot off. A backrun is then made. The opening in the three-way backrun valve between the top of the superheater and the washbox is closed and the connexion with the backrun pipe opened. Steam is introduced into the top of the superheater and passes down through the superheater, up through the carburettor, over into the top of the generator, and down through the incandescent fuel bed. In passing through the fuel bed, blue gas is formed which passes from the bottom of the generator through the backrun pipe, the three-way backrun valve, and the washbox into the relief holder. This operation continues for a slightly longer period than the uprun. It is followed by a very short uprun without introducing oil into the top of the carburettor. This completes an operating cycle which consists of a blow and a make period. These cycles are repeated throughout the 24 hours, if necessary, with intermissions only to add fuel to the generator or to clean the ashes from the generator grate.

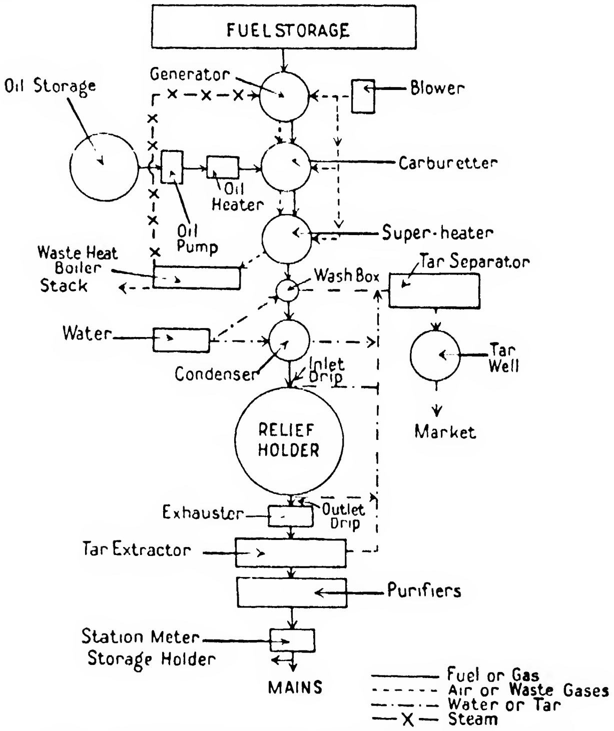


FIG. 2. Material flow sheet for carburetted blue-gas plant. (Morgan, *American Gas Practice*, vol. 1, 2nd ed., p. 454.)

The carburetted blue gas thus made must be purified before it can be utilized. This is done by pumping it from the relief holder with a gas exhauster and passing it through condensers and scrubbers to cool the gas and remove the tar. The gas then is passed through purifying equipment which removes all the hydrogen sulphide.

In many plants the hot-blast gases leaving the top of the superheater during the blow period are passed through a waste-heat boiler in which approximately 75% of the sensible heat in the blast gases is recovered as steam. Passing the hot carburetted blue gas through a waste-heat boiler has been tried but is not practical. Difficulty is encountered with the deposition and carbonization of tar in the gas flues.

Prior to the development of the backrun process by Young and Whitwell about 1920, the uprun was followed by a downrun in which steam was introduced into the top of the generator. The blue gas passed from the bottom of the generator up into the top of the carburettor and passed through the carburettor and superheater the same as the uprun gas. A system of hot valves was used in which the gas outlet at the bottom of the generator was closed when the gas outlet at the top of the generator was open and vice versa. With this arrangement it was not necessary to shut off the oil when making a downrun. The period of oil introduction was much longer than it is with the backrun operation.

Until 1918, coke or anthracite coal or a mixture of the two was used in the generator. The high prices of these fuels during the war forced gas companies to seek a cheaper fuel. High volatile coking coals were used. Their use resulted in an unbalanced heat condition in a carburetted blue-gas machine. The evolution of the volatile constituents of the coal during the blow period enriched the producer gas which caused excessive temperatures in the carburettor and superheater. Young and Whitwell conceived the idea of overcoming this difficulty by passing steam back through the superheater and carburettor. This operation has the following advantages as compared with the old uprun and downrun operation, not only with bituminous coal but also with coke or anthracite coal:

1. The overheating of the carburettor and superheater is overcome.
2. The excess heat is utilized in superheating the steam before passing through the fuel bed. This transfers the heat to the fuel bed and improves the blue-gas reaction.
3. The steam passing over the hot checker brick reacts with any carbon deposits thereby keeping the checker bricks clean.
4. The hot valves are not needed. This is a decided advantage in that they were a continual source of trouble.

A modern carburetted blue-gas machine with full automatic operation is truly a mechanical robot. Prof. Lowe, however, showed all the functions of the carburetted blue-gas process of to-day, except as these have been somewhat refined. The fundamental process remains much the same, but labour costs have made necessary mechanical devices which were not used at the start.

Carburetting Oils [13].

The composition of a carburetting oil depends mainly upon the composition of the crude oil from which it is made.

In the early days of the oil business, the products in most demand were the burning of lamp oils and the lubricating oils. Naphtha was a drug on the market and was used in some of the early processes to enrich manufactured gas. Gas oil was the distillate which was too heavy for lamp oil and not viscous enough for lubricating oil. It was difficult for the refiner to market and therefore available at a low price. Its low price in the early days was an important factor in the rapid development of the carburetted blue-gas process in the United States.

The enormous increase in the use of gasoline during the past 20 years with the resultant changes in refining practice has had a great influence on the composition of gas oil. Straight-run gas oil is now treated by cracking processes for the production of gasoline [2]. A large part of the gas oil now available for use in the manufacture of carburetted blue gas is the residue from the cracking process after the separation of gasoline and lamp oils.

With the continued increase in the demand for gasoline, there is less cracked gas oil available due to the practice of recycling the heavy distillates in the cracking processes. This scarcity of gas oil, resulting in increased prices, together with the increased production and use of natural gas, has led to the extensive use of heavy asphaltic oils for carburetting blue gas. These fuel oils may be in some cases crude oils which have such a small amount of low-boiling compounds that practically no gasoline can be obtained from them by straight distillation; they may be topped or stripped crude oil; or they may be the residue from a continuous distillation process.

Summing up, the carburetting material now used in the United States includes the following petroleum products:

A. Topped crudes obtained by the removal of naphtha from the original crude oil.
B. Stripped crudes which are produced when both naphtha and kerosine are removed.
C. Crude residues which are left when all but the high-boiling material is distilled from the crude.
D. Straight-run distillate (gas oil), the fraction of the crude distilling between 500° and 700° F. approximately.
E. Topped-cracked oil obtained by the removal of naphtha from oil which results when A, B, or D is subjected to a cracking process.
F. Cracked residue which is left when the distillate up to 500° F. is distilled from the cracked oil.
G. Cracked distillate, the fraction of the cracked oil which distils between 500° and 700° F. approximately.
H. Pressure distillate which is a fraction similar to G but separated from the cracked oil under pressure.

In general, when obtained from the same crude, the quality of these materials for carburetting decreases in the following order: D, B, A, C, G, F, E, H [5].

Characteristics of Carburetting Oils [14].

That the nature of a carburetting oil is complex and variable is obvious from its sources. Chemically the straight-run gas oils may be mixtures of compounds from any or all of the following series of hydrocarbons: paraffin, olefine, di-olefine, acetylene, naphthene, unsaturated rings, and aromatic compounds. In addition, the asphaltic fuel oils and the cracked residuums contain many complex hydrocarbons of whose nature there is little or no exact information. Some of the complex compounds of the heavy fuel oils also contain oxygen and sulphur.

Table V gives the characteristics of typical carburetting oils as shown by some of the tests commonly made on them.

The percentage of sulphur is important. The sulphur in the oil gas is a function of the sulphur in the oil. Since the sulphur as H_2S in the oil gas must be removed by purification, the higher the sulphur content of the oil the higher the expense of purifying the oil gas.

The percentage of hydrogen in an oil is a fair measure of its gas-making properties [33, 1934]. The higher the percentage of hydrogen in an oil, the greater the value for gas-making purposes.

The percentage of asphalt as well as that of coke, or carbon residue, is an indication of the tendency of the oil to deposit carbon in the carburettor.

The heating value of an oil is not a direct measure of its gas-making properties. It is useful, however, in calculating heat balances.

The flash- and fire-points are useful guides indicating the hazards of fire or explosion in the storage and use of an oil.

The gravity is expressed in degrees API. It gives little information about the nature or composition of a gas oil. For oils composed of the same series of hydrocarbons in the same proportions, the higher the API. gravity the lower the boiling-point. For oils of the same boiling-point or distilling between the same temperatures, those composed of paraffin hydrocarbons have the highest API. gravity, while the presence of unsaturated compounds or of ring compounds decreases the API. gravity.

TABLE V

Characteristics of Carburetting Oils. American Gas Practice

Morgan, 2nd ed., **1**, 462

Sample designation	*A* *Gas oil*	*C* *Gas oil*	*B* *Gas oil*	*1* *Heavy oil*	*2* *Heavy oil*	*3* *Heavy oil*	*4* *Heavy oil with some cracked tar*	*5* *Heavy oil containing cracked tar*
API. gravity at 77° F.	35·10	32·50	30·30	21·10	17·20	15·40	17·30	13·90
Coke, %	0·22	0·62	0·02	3·98	9·05	7·10	4·62	4·11
Sulphur, %	..	..	..	1·18	2 77	0·60	0·98	0·58
Distillation test:								
Per cent. by volume:								
Below 400° F.	1·30	1·40	0·90	..	..	..	..	..
400 to 450° F.	15·80	7·00	10·00	..	..	..	..	..
450 to 500° F.	26·00	15·30	26·00	..	0·60	..	4·50	3·90
500 to 550° F.	20·90	18·90	31·90	1·60	2·90	2·00	11·00	12·40
550 to 600° F.	14·80	17·40	16·70	5·20	5·60	4·30	12·40	16·00
600 to 650° F.	8·60	13·30	8·30	9·10	22·20	12·10	16·10	15·40
650 to 700° F.	6·70	9·50	2·50	26·80	24·20	31·90	14·40	16·00
700 to 750° F.	5·60	8·20	3·50	14·00	..	32·10	30·00	20·20
Residue and loss	0·30	2·00	0·20	43·30†	44·50‡	17·60	11·60	16·10
Below 600° F.	78·80	60·00	85·50	6·80	9·10	6·30	27·90	32·30
Above 600° F.	20·90	38·00*	14·30	49·90	46·40	66·10	60·50	51·60
Hydrocarbon test:								
Per cent. by volume:								
Paraffin	73·00	45·00	44·60	49·00	32·00	34·90	48·30	35·70
Naphthenes	9·00	19·00	43·00	23·00	48·00	36·30	21·70	27·90
Aromatics	4·00	10·00	8·00	8·40	0·80	12·00	12·00	14·40
Olefines	14·00	26·00	4·40	19·60	19·20	16·80	18·00	22·00
Saturated compounds	82·00	64·00	87·60	72·00	80·00	71·20	70·00	63·60
Aromatics and unsaturated	18·00	36·00	12·40	28·00	20·00	28·80	30·00	36·40
Cracking test:								
Optimum temperature, ° F.	1,330 1,390	1,380 1,425	1,380 1,410	1,350 1,500	1,350 1,450	1,300 1,450	1,350 1,450	1,300 1,425
B.Th.U. in gas per U.S. gal.	104,000	101,500	96,500	108,100	96,900	96,000	84,000	74,500
B.Th.U. of oil gas per cu. ft.	1,750	1,750	1,595	1,775	1,870	1,741	1,705	1,770
Cu. ft. of oil gas per U.S. gal.	59·50	58·00	60·50	60·80	51·80	55·10	49·30	42·00

* Includes 7·0% distilling between 750 and 817° F.

† Begins to crack at 705° F.

‡ Decomposes at 672° F.

In the distillation test, these determinations are made: the percentages by volume and the gravity of the fractions distilling between the points on the Fahrenheit scale which are multiples of 50°, and the residue left at 700° or 750° F. This test is very generally made on carburetting oil, and an effort has been made through a joint committee of the American Gas Association and the American Society for testing materials for this test and for other tests on gas oils [1, 1929].

Contrast between Gasification of Oil and Carbonization of Coal [15].

Coals are substances which contain considerable oxygen and yield two classes of compounds:

1. Phenols, containing oxygen, hydrogen, and carbon.
2. Hydrocarbons, containing only hydrogen and carbon.

In addition, coals contain appreciable amounts of nitrogen and sulphur; hence, the products of carbonization of coal always include ammonia, cyanides, hydrogen sulphide, complex nitrogen, and sulphur compounds. While the oils used in the carburetted blue-gas process usually contain some sulphur, they are generally free from oxygen and nitrogen, except in small amounts. Therefore, the products of the decomposition of oil by heat largely contain carbon and hydrogen, small amounts of hydrogen sulphide and smaller amounts of other sulphur compounds. With both coal and oil, considerable portions of the carbon and hydrogen are found free in the final products of decomposition.

In the carbonization of coal, the coal is gradually heated to the final carbonization temperature. The temperature is therefore continually changing. The final products are mixtures of both low temperature and high temperature. Furthermore, the decomposition of the hydrocarbons occurs in a constantly changing atmosphere in both character and amounts of diluents, hydrogen, water vapours, and oxides of carbon.

The decomposition of oil, a simpler material than coal, in the carburetted blue-gas process occurs in an atmosphere of blue gas and steam under fairly uniform conditions as to temperature and time of contact which are readily controlled.

Reactions in the Gasification of Oil.

In a carburetted blue-gas machine, oil is gasified by heat at practically atmospheric pressure (between 1 and 2 lb. per sq. in.).

Very little is really known about what actually occurs in the carburettor and superheater. The most extensive investigation on this subject is probably that of Whitaker and Leslie [32, 1916]. The purpose of their investigation was to show in general what results may be expected in the decomposition of an oil if temperature, rate of oil feed, and concentration of hydrogen are taken into account and carefully controlled. In addition to showing the proportions of products obtainable under a variety of conditions, Whitaker and Leslie reached the following conclusions as a result of their investigation:

I. That the importance of radiation in so far as it is concerned in the furnishing of the energy for the production of hydrocarbon reactions has been overestimated.

II. That effects often ascribed to catalysis are in reality due to effective heat transfer by conduction and convection from the large heated surfaces exposed to the gases.

III. That the equilibrium condition is not attained in a hydrocarbon system when an oil is decomposed by heat under conditions analogous to those of carburetted water-gas manufacture.

IV. That the course of the changes involved in the breaking down of a hydrocarbon may be roughly traced.

V. That hydrogen is produced from an oil even when the cracking takes place in hydrogen.

VI. That considerable absorption of hydrogen takes place when an oil is cracked in an atmosphere of hydrogen, and this absorption is greater the higher the concentration of hydrogen, the higher the temperature (within the range studied), and the lower the oil rate.

VII. That propylene and higher olefines constitute one-third by volume of the illuminants of the gas.

VIII. That the proportion of tar increases with decrease in temperature, and with increasing oil rate, particularly at the lower temperatures.

IX. That no marked and consistent difference in the amount of tar formed when an oil is decomposed alone or in hydrogen at temperatures of 723° C. or below is noticeable. At 825° C. less tar is formed when the oil is cracked in hydrogen. The tars formed below 723° C. are in large part ununchanged or partly changed oil, whereas those tars formed above 800° C. are essentially composed of synthetic products.

X. That the reactions which result in decreasing the proportion of illuminants are the most rapid.

XI. That the presence of hydrogen during the decomposition of an oil has the effect of increasing largely the proportion of the carbon of the oil appearing as hydrocarbons in the gas.

XII. That within the temperature range studied the volume of illuminants produced per volume of oil increases with one slight exception. The formation of methane is greater the higher the temperature. The formation of ethane is not large at any temperature and therefore the primary decomposition of an oil involves chiefly a splitting off of methane rather than ethane or higher homologues.

XIII. That a temperature of 823° C. is desirable in decomposing an oil, provided that too great opportunity for extensive secondary and tertiary change is not given.

XIV. That with correct design of apparatus, and proper adjustment of temperature, rate of oil feed, and concentration of hydrogen, it is possible to obtain gases of widely varying composition.

The oil used in this investigation was a water-white oil of 0·800 specific gravity which boiled between 150° C. and 265° C. Since Whitaker and Leslie state that the plan and scope of their work was to study the decomposition of paraffin hydrocarbons, it is probably fair to assume that the oil was a paraffin oil.

Practically all the work that has been done on the reactions occurring in the gasification of oils in connexion with the manufacture of gas has been on paraffin oils. Regardless of the oil used or the nature of the reactions that occur, the final results are production of free hydrogen: simple gaseous hydrocarbons (methane, ethane, ethylene, and propylene), tar containing aromatics and heavy complex hydrocarbons, and free carbon. If the original oil consists of paraffins and olefines, the result is less free carbon and tar, more and a better gas containing less free hydrogen, and more hydrocarbons. If the oil is composed of ring compounds, either naphthenes or unsaturated rings, the result is more free carbon and tar, less gas and a leaner gas containing more free hydrogen and less hydrocarbons. Although the percentage of hydrogen in the oil is an indication of its gas-making properties, it is the amount of carbon in the hydrocarbons of the gas that is the final measure of the enriching value. This depends upon both the nature of the oil and the conditions under which it is gasified [16].

In a modern carburetted blue-gas machine using the backrun, the oil is gasified contrary to the counterflow principle. It is sprayed into the top of the carburettor where the temperature of the checker brick is the highest, and the oil gas leaves the machine at the top of the superheater where the temperature is the lowest. The variation in temperature between these two points is 200° F. or more. A high temperature in the top of the carburettor is essential to vaporize the oil. From the standpoint of gas making, the ideal goal is complete gasification of the oil without the production of tar or lampblack. The author (Willien) believes that this goal will be more nearly reached if the oil is cracked or gasified according to the counterflow principle. This will probably require vaporizing the oil before introducing it into a carburetted blue-gas machine and may also require extensive changes to a standard carburetted blue-gas machine or a machine of an entirely new design. The coke residue remaining after vaporization when using fuel oil will fill a vaporizing chamber very quickly. With present practice the coke is deposited on the checker brick and burned off during the blow period and gasified by the steam during the backrun.

There should be more research work done on the reactions that take place when oil is gasified in a carburetted blue-gas machine.

Factors influencing Gasification of Oil.

Among various manufacturing processes, and particularly among those concerned with the production of manufactured gas, there is probably none so complicated and subjected to so many variable factors as that involved in the manufacture of carburetted blue gas. Harper [9,1919] listed 289 gas-machine factors involved in the manufacture of carburetted blue gas. These factors involve not only the gasification of oil but also the production of blue gas, machine outputs, &c.

The primary factors in the gasification of oil are:

1. Temperature.
2. Time of contact.
3. Concentration or presence of foreign or diluent gases.

Pressure is not an important factor in the carburetted blue-gas process because there is practically none in a carburetted blue-gas machine.

Temperature. The temperature at which an oil is gasified is of primary importance.

Excessive temperatures in the carbutettor and superheater cause the formation of lampblack and naphthalene which clog pipes and equipment around a gas plant. If allowed to pass into a gas-distribution system, naphthalene will deposit in the pipes and cause stoppages.

With low temperatures, there is incomplete gasification of the oil resulting in the production of an excessive amount of an oily tar. The oil gas will contain liquid phase gum-forming constituents which are deposited and cause stoppages when the gas passes through a restricted area as in a pressure regulator, or a small orifice such as a pilot light on a gas appliance.

The proper cracking temperature obviously is that at which the maximum carburetting efficiency is obtained. While it varies with the character of the oil used and is dependent upon several other factors, in general the temperature used is approximately 1,400° F. (760° C.) as measured at the base of either the carburettor or superheater.

In the operation of a carburetted blue-gas machine, two methods are used for determining whether the oil is being cracked properly. One is the trowel test in which gas is allowed to flow from a small cock at the top of the superheater and impinge on a mason's trowel or a piece of bright metal. If the tar deposited on the metal is of an oily nature, the temperature is too low; if lampblack is deposited, the temperature is too high. The proper temperature is that which produces a dark brown deposit free from oil and lampblack. The test may also be made with a strip of unglazed white paper. The other method is the appearance of the tar overflowing with the water from the wash-box. With low temperatures the tar will contain appreciable amounts of undecomposed oil which float on the surface of the water. With excessive temperatures there will be a scum of lampblack. At the proper temperature there will be a dark brown tar which will float just below the surface of the water.

Time of Contact. The principal factors influencing the time of contact are:

1. The rate of oil input.
2. The rate of blue-gas production.
3. The amount of checker bricks, their arrangement and spacing in the carburettor and superheater.

At a given temperature and time of contact, which we will assume to be proper for the most efficient cracking of a given oil, an increase in the time of contact should result in overcracking of the oil, while a decrease in the time of contact should result in undercracking. While this is true to a certain extent in the carburetted blue-gas process, a variation in temperature produces a more decided effect than a proportional variation in the time of contact without a variation in temperature.

Many of the improvements and changes that have been made in the carburetted blue-gas machine during the past 20 years have resulted in increased gas-generating capacity, the tendencies of which have been towards a reduction in the time of contact. With the introduction of the back-run process the period of oil introduction was reduced approximately 50%, which reduced the time of contact a proportionate amount. While there has been a slight increase in the temperature carried in the carburettor and superheater—about 15%—there has been no decrease in the carburetting efficiencies of the oil. Whatever change that has occurred has been towards greater efficiencies rather than less. This statement is based upon the assumption that the same oil is used. Lower carburetting efficiencies are obtained with the fuel or bunker oils used to-day than with a gas oil.

A small amount of gas usually leaks around the stack valve of a carburetted blue-gas machine during the run- or gas-making period. This gas is ignited by a pilot flame. From the character of the gas flame at the stack valve the presence of oil gas can be determined. Assuming the time of contact in a carburetted blue-gas machine to be the time from the turning on of the oil into the top of the carburettor to the time of the oil gas appearing at the stack valve, readings taken by the author (Willien) showed the time of contact to be between 5 and 6 seconds.

Tests were made by the author (Willien) in which the temperature at the base of the superheater was maintained constant and the rate of oil introduction was increased as much as 40%. This reduction in the time of contact had no appreciable effect on the carburetting efficiency of the oil.

Concentration or Presence of Foreign or Diluent Gases. Downing and Pohlmann [4, 1916] made an extensive series of tests in which a gas oil was cracked in several different atmospheres in a laboratory oil-cracking machine. The oil was cracked at various temperatures in atmospheres of the following gases: nitrogen, oil only, carbon dioxide, carbon monoxide, hydrogen, methane, blue gas, blue gas plus 10% steam, and blue gas plus 20% steam. A summary of these tests is given in Table VI.

The results of these tests lead to the conclusion that no advantage is to be gained over the blue-gas atmosphere. The tar formation was lower and carbon deposition medium. The B.Th.U. results were greater than those obtained in any single atmosphere except that of blue gas plus 10% and 20% steam. The oil cracked in such an atmosphere showed greatly increased B.Th.U. in the oil gas produced per U.S. gallon of oil at temperatures from 1,225° to 1,475° F. This may have been due to a decrease in an excessive time of contact, to some reaction between the steam and oil, and to a reaction between the steam and the carbon deposited in the cracking tube. Such an atmosphere more nearly approaches that of actual practice than the atmosphere in any of the other tests. An appreciable percentage of the steam passing through the incandescent fuel bed in the generator is not converted into blue gas.

This undecomposed superheated steam passes over into the carburettor with the blue gas. In reality, therefore, the oil is cracked in an atmosphere of a mixture of blue gas and steam.

The oil used by Downing and Pohlmann was a Mid-Continental gas oil of 0·8614 gravity, 93% of which distilled up to 700° F. When cracked straight at temperatures between 1,300° and 1,350° F., between 78,000 and 80,000 B.Th.U. was recovered as an oil gas having a heating value of between 1,200 and 1,300 B.Th.U. per cu. ft. from a gallon of oil. These results compared very favourably with the results of an extensive series of plant tests made at San Rafael, California, in May 1932 [10, 1932]. In these tests 11,550,000 cu. ft. of oil gas was made with an average heating value of 955 B.Th.U. per cu. ft. While the oil was cracked in the presence of some steam, an average of 79,500 B.Th.U. was recovered as oil gas from a gallon of oil. The oil used at San Rafael was known as Diesel oil, a distillate from a California oil. Its gravity was 0·870 and on distillation 99% distilled up to 723° F. (384° C.).

Summing up the effects of cracking atmospheres in the manufacture of carburetted blue gas, the cracking of oil in an atmosphere of blue gas and steam produces the following results [17]:

1. Increases the amount of hydrocarbons in the gas.
2. Decreases the formation of lampblack and tar.
3. Permits higher temperatures to be carried in the carburettor and superheater without the formation of excessive amounts of naphthalene and lampblack.

TABLE VI

Results on Cracking Gas Oil in Atmospheres of Various Gases

Downing and Pohlmann. *Proc. Amer. Gas Institute*, 610, Table III (1916)

Kind of diluent	*Nitrogen*		*Oil only*		*Carbon dioxide*		*Carbon monoxide*		*Hydrogen*			*Methane*	
Temperature, ° F.	1,304	1,349	1,315	1,349	1,300	1,350	1,305	1,358	1,302	1,355	1,416	1,300	1,349
Cu. ft. oil gas per U.S. gal. oil	58·50	61·20	62·60	66·20	66·00	66·20	57·80	63·70	50·20	53·60	55·80	57·20	61·90
1,000 B.Th.U. per U.S. gal.	90·70	98·50	79·90	78·00	99·40	97·50	91·60	96·10	93·00	99·20	99·90	88·00	96·00
Per cent. tar	38·00	34·80	43·80	32·00	37·50	29·40	41·20	38·10	30·40	27·50	27·10	33·90	32·50
Per cent. carbon	12·70	16·20	12·40	15·80	20·20	24·30	5·20	8·70	7·10	6·70	8·70	14·20	11·90
Per cent. gas	49·30	49·00	43·80	46·20	42·30	46·30	53·60	53·20	62·50	65·80	64·20	51·90	55·60
Constituents formed, per gal. oil:													
Cu. ft. illuminants	25·60	27·00	19·40	18·15	28·26	27·25	30·00	29·80	24·50	26·00	25·20	27·00	28·90
Cu. ft. carbon monoxide	2·60	1·60	1·25	1·06	3·39	2·96	−5·00	−2·90	2·90	1·00	2·00	3·30	1·80
Cu. ft. hydrogen	8·50	10·60	8·20	10·00	6·71	5·04	0·30	8·10	−13·10	−20·60	−17·80	8·10	10·20
Cu. ft. methane	21·30	27·00	32·42	35·80	30·29	29·05	30·20	28·20	13·30	32·30	36·90	17·40	17·20
Cu. ft. ethane	2·40	1·00	..	..	..	..	..	..	19·40	12·60	9·40	0·20	..
B.Th.U. of illuminants	2,370	2,260	2,260	2,580	2,330	2,410	2,090	2,200	2,090	2,020	2,160	2,466	2,585
Sp. gr. of illuminants	1·162	1·182	1·112	..	1·170	1·100	1·151	1·203	0·989	0·974	0·965	1·097	1·098

Kind of diluent	*Blue gas*					*10% steam*				*20% steam*			
Temperature, ° F.	1,212	1,256	1,315	1,357	1,452	1,250	1,300	1,350	1,400	1,300	1,250	1,400	1,450
Cu. ft. oil gas per U.S. gal. oil	32·60	45·90	53·20	56·60	59·80	54·20	56·60	60·40	65·20	59·20	61·80	61·70	66·80
1,000 B.Th.U. per U.S. gal.	67·75	92·10	99·80	100·75	103·30	98·70	100·70	101·60	102·00	107·20	110·70	105·50	105·50
Per cent. tar	48·80	37·60	31·80	30·30	26·00	29·50	24·20	23·90	24·30	20·60	25·60	21·20	20·20
Per cent. carbon	12·80	9·50	11·40	10·50	17·10	11·20	15·20	18·10	18·30	5·90	5·40	14·80	14·80
Per cent. gas	38·40	52·90	56·80	59·20	56·90	59·30	60·60	58·00	57·40	73·50	69·00	64·00	65·00
Constituents formed, per gal. oil:													
Cu. ft. illuminants	19·40	27·60	30·00	29·80	27·40	27·40	27·37	26·46	25·81	28·20	29·50	27·40	26·40
Cu. ft. carbon monoxide	+0·60	−1·10	+1·40	−0·60	−1·10	−1·51	−0·50	+1·17	+1·50	+0·60	−0·20	+0·90	−0·80
Cu. ft. hydrogen	−3·40	−6·40	−6·00	−9·10	−11·40	−8·08	−8·10	−12·10	−9·18	−3·20	−9·10	−6·10	−2·70
Cu. ft. methane	13·80	21·90	26·80	32·30	44·90	26·00	32·52	39·80	44·04	36·20	36·50	29·60	35·40
Cu. ft. ethane	1·60	1·90	4·50	4·90	..	6·18	3·08	0·62	..	..	3·80	7·00	6·00
B.Th.U. of illuminants	2,670	2,492	2,243	2,045	2,211	2,370	2,370	2,405	2,320	2,541	2,440	2,342	2,379
Sp. gr. of illuminants	1·270	1·245	1·273	1·189	1·158	1·200	1·192	1·04	1·025	1·382	1·01	1·01	0·988

Carburetting Efficiencies.

In carburetted blue-gas manufacture the carburetting efficiency is spoken of as 'Oil Efficiency'. It is expressed as B.Th.U. per gallon of oil (in England it is therms per gallon—a therm is 100,000 B.Th.U.), and is the number of B.Th.U. per gallon of oil which appear in the heating value of the oil gas in the final carburetted blue gas.

When carburetted blue gas was made on a candle-power standard, the carburetting efficiency was expressed as candles per gallon. It was determined by dividing the gallons of oil used per 1,000 cu. ft. of carburetted blue gas into the candle-power of the gas. Since blue gas has very little or no illuminating value, the illuminating value of the candle-power of carburetted blue gas is due entirely to the oil gas. The candles per gallon, therefore, was a rational measurement of the carburetting efficiency.

While blue gas has little or no illuminating value, it has a heating value of approximately 285 B.Th.U. per cu. ft. In a carburetted blue gas of 550 B.Th.U. per cu. ft. about 40% of the heating value is due to the blue gas and 60% is due to the oil gas. It is apparent therefore that in order to determine or calculate the oil efficiency when making carburetted blue gas to a heating value standard the following data must be available:

1. The B.Th.U. per cu. ft. of the final carburetted blue gas—*A*.
2. The gallons of oil used per 1,000 cu. ft. of carburetted blue gas—*B*.

3. The B.Th.U. per cu. ft. of blue gas—*C*.
4. The cu. ft. of oil gas made per U.S. gallon of oil used—*D*.

With this data, the oil efficiency can be calculated as follows:

Per cent. of oil gas—$B \times D/1{,}000$.
Per cent. of blue gas—$100-(B \times D/1{,}000)$.
B.Th.U. due to blue gas—$C \times \%$ of oil gas.
B.Th.U. due to oil—$A-$B.Th.U. due to blue gas.
Oil efficiency—B.Th.U. due to oil/*B*.

This method was used for calculating oil efficiencies up to about 1925. Assumed values for *C* and *D* were used varying from 60 to 80 for *D* and from 290 to 300 for *C*. Since both of these factors are variables, especially *D*, the results were nothing more than an approximation.

Frank Wills [6, 1924], of the Pacific Gas and Electric Company, developed a method for calculating—from an analysis of the gas—the following components in oil gas made by the Pacific Coast Oil Gas Process:

1. Air.
2. Combustion products.
3. Blue gas.
4. Oil gas.

Using the Wills method, it is also possible to calculate the composition and heating value of the blue gas and the oil gas.

In 1925 the first attempt was made to apply the Wills method for calculating the oil efficiency in carburetted blue-gas operation [34]. In 1926 a Sub-Committee on Uniform Oil Efficiency was appointed by the Technical Section of the American Gas Association to study the question and recommend a uniform formula or method for calculating oil efficiencies. This Committee functioned for 2 years and finally recommended the adoption of the Pacific Coast method with the Providence modification as the official method for calculating oil efficiencies for straight carburetted blue-gas operation with anthracite coal or coke [28, 1927]. In the summary of the Committee's report of 1927, the following statements appear:

1. 'The Pacific Coast Method with the Providence Modification is the best method for calculating oil efficiencies with straight water gas operation with coke and anthracite coal.'
2. 'When using bituminous coal with the blow-run there are too many variables to make it possible to calculate oil efficiency with any degree of accuracy by any known method.'

The Pacific Coast Method is based upon the method developed by Frank Wills. The following data are necessary for its application:

1. An average analysis of the carburetted blue gas.
2. The average B.Th.U. per cu. ft. of the carburetted blue gas determined with a gas calorimeter.
3. The gallons of carburetting oil used per 1,000 cu. ft. of the carburetted blue gas.

The gas analysis is separated into four parts, as follows:

1. *Air.* The percentage of air in the gas is equal to five times the percentage O_2 shown in the gas analysis.

2. *Combustion Products.* These are the products of combustion in a carburetted blue-gas machine at the end of the 'blow'. They are carried forward with the carburetted blue gas made during 'the uprun' and appear in the final finished gas. The combustion products consist of CO_2 and N_2. Their percentages are calculated from the N_2 in the gas. The N_2 in the combustion products is the difference between the total N_2 shown in the gas analysis and four times the O_2. A large number of stack gas analyses showed that the ratio of N_2 to CO_2 was six to one (burning oil). The CO_2 in the combustion products is therefore taken as one-sixth the calculated N_2 in the combustion products. The percentage of combustion products is the sum of the N_2 and CO_2 thus calculated. (With solid fuel the ratio of N_2 to CO_2 is four to one.)

3. *Blue Gas.* This consists of CO, CO_2, and H_2. All of the CO in the carburetted blue gas is assumed to come from the blue-gas reaction. The CO_2 due to the blue-gas reaction is the difference between the total CO_2 in the finished gas and the CO_2 in the combustion products. In the blue-gas reaction equal volumes of CO and H_2 are produced and for every volume of CO_2 produced two volumes of H_2 are produced. The H_2 due to the blue-gas reaction is therefore taken to be the sum of the CO plus $2CO_2$. The percentage of blue gas is the sum of the CO shown in the gas analysis and the calculated amounts of CO_2 and H_2.

4. *Oil Gas.* This is calculated as the difference between 100 and the sum of the calculated percentages of air, combustion products, and blue gas.

From the percentage of CO in the final gas and the calculated percentage of H_2 due to the blue-gas reaction, the B.Th.U. in the final gas due to the blue gas can be calculated. The difference between this B.Th.U. and the average B.Th.U. of the carburetted blue gas represents the B.Th.U. due to the carburetting oil. The oil efficiency is then determined by multiplying the B.Th.U., due to the carburetting oil, by 1,000 and dividing by the gallons of oil used per 1,000 cu. ft. of carburetted blue gas.

The Providence Modification is a correction of the calculated B.Th.U. due to the blue gas for the presence of a small amount of CH_4 in blue gas made from coke. Blue gas thus made contains about 1% of CH_4. L. E. Knowlton [27, 1925] of the Providence Gas Company, Providence, Rhode Island, found that when making straight blue gas the actual heating value as determined with a gas calorimeter averaged about 8 B.Th.U. higher than that calculated as above. He suggested, therefore, that the calculated heating value of the blue gas be corrected by adding to it an amount equal to the calculated percentage of blue gas times 8 divided by 100.

Pexton [25, 1929] has shown that blue gas made from coke contains H_2 liberated from the coke which amounts to 2·6% more than that calculated from the percentages of CO and CO_2. This would increase the heating value of the blue gas by about 3%. Pexton also points out that the percentage of blue gas can be calculated by an O_2 balance, thereby eliminating the calculation of combustion products. By the O_2 balance method one-quarter the N_2 found by analysis in the carburetted blue gas is taken as O_2 supplied by air. This amount of O_2 subtracted from the total free and combined O_2 in the gas is the O_2 derived from steam. The volume of H_2 in the blue gas is twice the volume of O_2 from the steam. From the percentage of CO in the finished gas and the calculated H_2 in the blue gas, the heating value due to the blue gas can be calculated. To this calculated heating value may be added an allowance for both the CH_4 and the H_2 from the coke.

The following is a list of the data which it is possible to determine by the Pacific Coast Method:

1. Per cent. of air in finished gas.
2. Per cent. of combustion products in finished gas.
3. Per cent. of blue gas in the finished gas.
4. Per cent. of oil gas in the finished gas.
5. Heating value of blue gas.
6. Heating value of oil gas.
7. B.Th.U. in finished gas due to blue gas.
8. B.Th.U. in finished gas due to oil gas.
9. B.Th.U. imparted to finished gas per U.S. gallon of oil used.
10. Cu. ft. of oil gas made per U.S. gallon of oil.
11. Per cent. of steam decomposed.
12. Pounds of carbon used per 1,000 cu. ft. of carburetted blue gas, exclusive of carbon used during the blowing period.
13. The extent of H_2 absorption or formation in the oil-cracking process.

The method is also valuable in comparing the operating results of different gas plants.

Mention was made of the inability to use the Pacific Coast Method when a blow-run is used. A blow-run is a modification in the operation of a carburetted blue-gas machine. At the end of the blow period the air entering the crossover connexion between the generator and carburettor is shut off and the stack valve is closed. Air continues to enter the bottom of the generator, passes up through the fuel bed and forms a low-grade producer gas. This gas passes through the carburettor, superheater, and wash-box into the relief holder, where it mixes with carburetted blue gas. This operation continues for only a few seconds.

An air purge is frequently used. It is made at the end of the make period just before going on to a blow. After shutting off the steam entering the bottom of the generator for the final short uprun of the make period, air is introduced into the bottom of the generator. It passes up through the fuel bed and into the relief holder the same as in the blow-run. This operation is usually shorter than the blow-run. Its object is to purge the machine of the blue gas remaining in it from the final short uprun of the make period.

Both the blow-run and air-purge gas contain a large percentage of N_2, some CO_2, and CO. The finished carburetted blue gas, therefore, contains appreciable amounts of these gases which cannot be classed as air, combustion products, or blue gas. It is for this reason that the Pacific Coast Method cannot be used for calculating oil efficiency when either a blow-run or air-purge is used in the manufacture of carburetted blue gas.

When bituminous coal is used in the generator of a carburetted blue-gas machine, either straight or mixed with coke, about 58% of the coal gas liberated is recovered in the finished carburetted blue gas [22, 1926]. It constitutes about 7·8% by volume of the finished gas and contributes about 8·4% of the heating value of the finished gas. This fact, together with the fact that a blow-run is usually used with bituminous coal operation, makes it impossible to use the Pacific Coast Method for calculating oil efficiencies.

The oil efficiencies obtained with normal carburetted blue-gas operation will average about 105,000 B.Th.U. per U.S. gallon with gas oil and about 90,000 to 95,000 B.Th.U. with fuel oil.

Believing that the ratio between the percentages of saturated and unsaturated hydrocarbons, as determined by a gas analysis, is an indication whether an oil is being cracked at its maximum efficiency in a carburetted blue-gas machine, a study of this subject was made [35, 1934]. If such a ratio is constant or very nearly so, when an oil is cracked most efficiently the operation of a carburetted blue-gas machine can be checked by calculating such a ratio. If the ratio is less than that for the maximum cracking efficiency it will indicate that the oil is insufficiently cracked. If the ratio is greater, the oil is overcracked. The former indicates low-cracking temperature while the latter indicates excessive temperature. The results of this study indicate that the ratio between the proportions of saturated and unsaturated hydrocarbons in the oil gas is no criterion for determining the efficiency at which an oil is being cracked in a carburetted blue-gas machine.

Evaluation of Carburetting Oils [18].

While a plant test really gives the final answer in evaluating an oil, the desirability of laboratory tests which will give some indication of the plant results that may be expected has been recognized. Considerable work has been done on the development of such laboratory tests. These tests may be classed as:

1. Chemical.
2. Distillation.
3. Cracking.

Chemical tests are the determination of the percentages of the various groups of hydrocarbons such as unsaturates, aromatics, and naphthenes and paraffins. The expected efficiency is then computed from factors assigned to the different groups of hydrocarbons [31, 1927–30].

These tests are usually applied to ordinary gas oils. When attempts are made, however, to apply them to the asphaltic fuel oils and cracking still residues, it has not been definitely determined whether to make them on the original oil as received, or the distillate obtained from it. If a distillate is used, should it be obtained by distilling up to the temperature at which cracking begins, or by distilling to a coke residue.

The amount of an oil distilling up to 600° F. gives some idea of its carburetting value. The portion distilling below 600° F. is more valuable for gas-making purposes than that distilling above 600° F. If a considerable portion of the oil distils above 600° F., the higher the specific gravity of this portion the lower the carburetting value of the oil [26, 1930].

The laboratory cracking test is an attempt to reproduce on a small scale the temperatures and other conditions under which the oil is gasified in plant operation. Downing and Pohlmann [4, 1916] were the first to develop such a test. Their apparatus with slight modifications is the one commonly used. The oil is gasified in a heated steel pipe in an atmosphere of blue gas. The carburetted blue gas passes through condensing and purifying apparatus, is measured and stored in a small holder from which it is sampled for analysis and other tests.

Murphy [23, 1930] introduces water into the cracking tube in order to gasify the oil in an atmosphere of blue gas and steam. This reproduces more nearly the conditions existing in the plant apparatus where excess steam, as well as blue gas, is always present in the carburettor and superheater.

Dick [3, 1933] developed a laboratory cracking furnace for heavy oils and gas oils. The oil is automatically fed into a vertical tube and cracked in an atmosphere of hydrogen.

The results of laboratory cracking tests show:

1. The B.Th.U. recovered in the gas per gallon of oil.
2. The cubic feet of oil gas produced per gallon of oil.
3. The heating value of the oil gas produced.

Such tests are usually made at two or more different temperatures in order to obtain an idea of the optimum operating temperature. While a fair degree of accuracy can be obtained in a laboratory cracking test, it is not to be expected that the results will be exactly duplicated under plant conditions. They do give valuable indications of the carburetting values, and when used by a person experienced in translating them they show quite accurately the relative values of different oils and also serve as a guide to the proper operating conditions for obtaining the best results with a given oil.

Refinery Oil Gas.

The development of oil-cracking processes for the production of gasoline has resulted in the production of a large volume of high-heating value oil gas by a by-product. While this gas is generally used for fuel purposes in oil refineries, at times it can be replaced with other fuels and the oil gas sold to gas companies for use in the manufacture of city gas.

Fig. 3 is a material flow sheet for the U.G.I. Reforming Process. Where refinery oil gas is used for such purposes, part of it is reformed and part is used for cold enrichment. The reforming is done in a standard three-shell carburetted blue-gas machine with a process developed by the United Gas Improvement Company. The oil gas, together with steam, is passed through the incandescent fuel bed in the generator. The gas produced by this reforming process closely resembles coal gas. While a considerable amount of lampblack is actually formed in the process, the operation is so controlled that practically none of it is carried forward with the reformed gas [29, 1930–1].

Low-gravity Carburetted Blue Gas.

For mixing with coal gas it is frequently desirable to make a carburetted blue gas having a lower specific gravity than that made with normal operation which is about 0·65. Such a gas is made by the Low Gravity Water Gas Process [37, 1927–30].

An oil spray is installed in the top of the superheater of a carburetted blue-gas machine equipped for backrun operation. During the backrun portion of the operating cycle oil and steam are introduced into the top of the superheater. In passing down through the superheater and up through the carburettor the oil is gasified. The oil gas and steam then pass down through the incandescent fuel bed in the generator. The steam forms blue gas and oil gas is reformed or cracked from about 1,200 B.Th.U. per cu. ft. to about 500 B.Th.U. In the reforming, considerable hydrogen is made, thereby increasing the percentage of hydrogen in the finished gas and reducing the specific gravity. This process, known as the Willien-Stein Process, is controlled by the United Gas Improvement Company.

Fuel or Bunker C Oils [30, 1924–34].

In the use of fuel or bunker C oils for carburetting purposes in the manufacture of carburetted blue gas, a portion of the oil is reformed by spraying it into the top of the generator during the backrun. Very few or no checker bricks are used in the carburettor. During the uprun, in some instances, oil is introduced into the tops of both the generator and carburettor. The reason for doing so is to prevent excessive deposits of coke on the checker bricks.

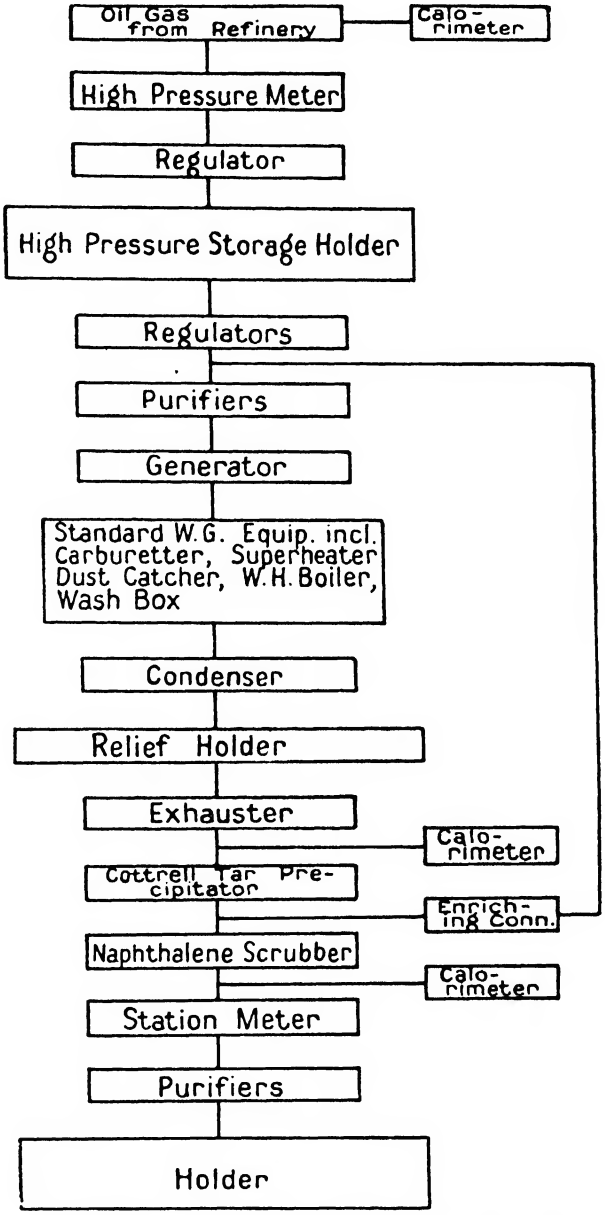


FIG. 3. Material flow sheet for U.G.I. refinery oil-gas reforming process.

If sprayed into the top of the generator the coke is deposited on the fuel bed and finally gasified along with the generator fuel. The oil sprayed into the top of the carburettor, with very few or no checker bricks, is vaporized and the coke is deposited in the bottom of the carburettor, the crossover connexion, and the bottom of the superheater. The accumulated coke is removed periodically.

Oil Gas—Pacific Coast Process

The production of oil gas has been largely limited to the Pacific Coast. Lack of supply of solid fuels such as coal or coke, except at prohibitive prices, and the existence of an abundant supply of petroleum in Southern California led to the development of the Pacific Coast Oil Gas Process.

The early oil-gas process patents were issued in 1889 to L. P. Lowe, son of Prof. T. S. C. Lowe, who invented the carburetted blue-gas process. While some small Lowe crude oil water-gas generators were built in the nineties, it was not until the first decade of 1900 that large machines were built. The improvements in the process that made large units practicable were due in part to E. C. Jones, for many years Chief Engineer, Gas Department, of the Pacific Gas and Electric Company; and the most generally used two-shell oil-gas generator bears his name. Further improvements were made by his son, L. B. Jones.

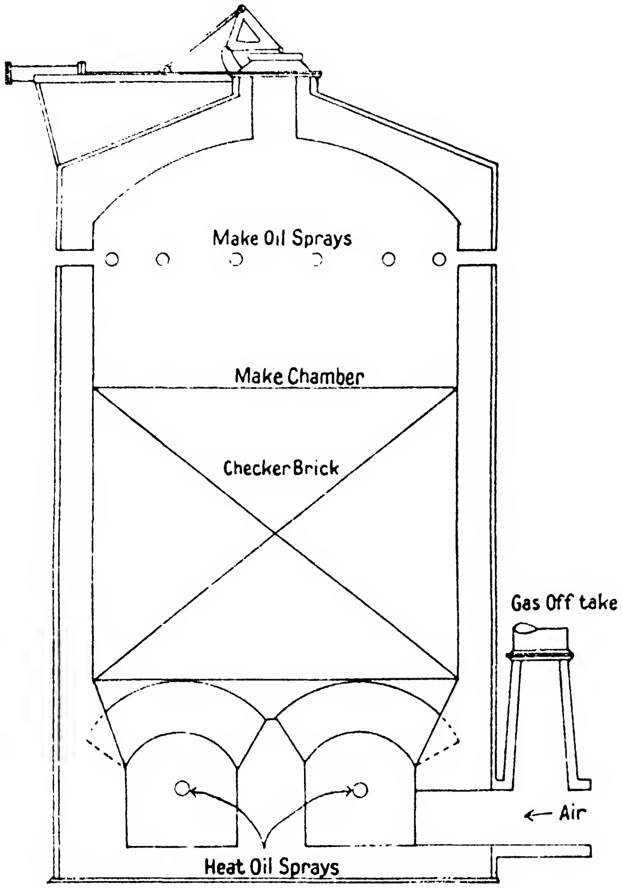


FIG. 4. Single-shell oil-gas machine.

The oil-gas process is similar to the carburetted blue-gas process in that it is an intermittent process consisting of alternate heating- and gas-making periods, blow and run. No solid fuel is used, only oil and steam.

Two types of oil-gas machines are used:

1. The single-shell straight-shot machine.
2. The two-shell Jones machine.

Single-shell Machine. Fig. 4 shows a single-shell straight-shot machine. It is a cylindrical steel shell lined with fire brick. On the bottom across the centre of the generator is a brick wall from which arches are sprung to the side walls which carry the checker brick. The space under the checker brick arches constitutes an offtake chamber as well as a combustion chamber. There are two air-inlet connexions to the combustion chamber above which connexions are two nozzles for the heating burners. The gas offtake connexion is also at the bottom between the air connexions. It is brick-lined into the wash-box. There is a stack valve at the centre of the top. From 12 to 24 oil sprays enter the shell just below the tiled crown, which is made as flat as possible to obtain the maximum amount of vapour space between the sprays and checker brick.

There are several sizes of single-shell machines used. The largest ones having a rated capacity of 5 to 6 million cubic feet of gas per day are 27 ft. in diameter and 43 ft. 3 in. high. They contain from 70,000 to 85,000 checker bricks.

Two-shell Jones Machine (see Fig. 5). It consists of two cylindrical steel shells lined with fire bricks, and carrying checker bricks on refractory arches. The two shells are known as the primary and secondary generators. The largest machines, with a rated capacity of 5–6 million cubic feet of gas per day, have two 18 ft. 9 in. diameter shells. The primary generator, with a blast inlet on top, is from 47 ft. 7 in. to 49 ft. high, and the secondary generator, with the stack valve on top, is from 57 ft. 4 in. to 63 ft. high. There are five sections of checkerwork, two in the primary generator and three in the secondary. These sections contain a total of from 46,000 to 52,000 checker bricks.

On the bottom, across the primary generator, are a series of brick piers joined by tiles, upon which are supported the checker bricks of the primary making chamber (about 17,000 checker bricks). Above these checker bricks a series of arches is sprung from wall to wall which carry about 4,000 checker bricks and form the primary superheater.

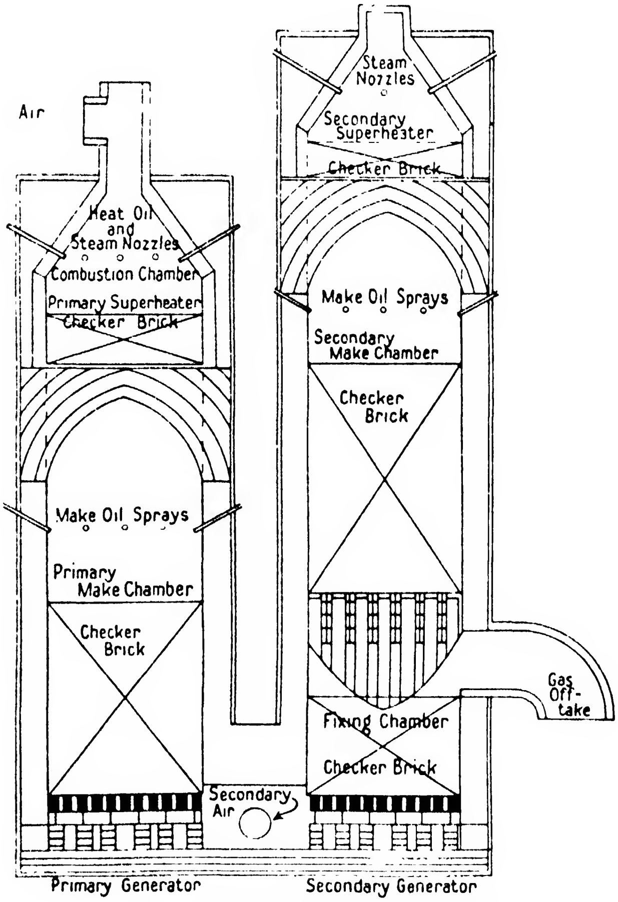


FIG. 5. Two-shell Jones oil-gas machine.

The secondary generator also has a row of bottom piers supporting about 12,000 checker bricks which constitute a fixing section for the gas produced in the primary generator. Between the top of these checker bricks and the first series of arches is the gas offtake chamber, containing the outlet to the wash-box. This set of arches supports the checker bricks (about 17,000) of the secondary make chamber. Above this section is a second set of arches supporting the checker bricks (about 4,000) of the secondary superheater. All checker bricks are arranged in flues, not staggered, with approximately 3-in. spacing.

An air-blast connexion is made to a tee on top of the primary generator, and a secondary air connexion is made at the base of the secondary generator. At the top of the primary generator and encircling it are 8 heating oil sprays and 4 steam nozzles. Each making chamber is encircled with 14 make-oil injectors. All oil is injected with steam atomizing sprays. (No atomizing sprays have been used successfully.)

Outline of Process. As previously stated, the oil-gas process is similar to the carburetted blue-gas process in that it consists of alternate heating and gas-making periods. In the carburetted blue-gas process, a producer gas is made by blasting a bed of solid fuel, thus raising its temperature, and then burning the producer gas with secondary air in the carburettor and superheater checker brick. In the oil-gas process heat storage is entirely in the refractory walls, arches, and checkerwork.

The same oil is used for both heating and gas making. It is a refinery residuum oil of an asphaltic base, the gravity of which ranges from 16 to 19° API. Upon distillation, about 60% distils between 662 and 752° F. with up to 8% coke residue. The sulphur content is from 0·7 to 1·7% by weight.

Single-shell Machine. The operating cycle varies from 30 to 36 min. The heating period is about 30% of the cycle and the make period about 70%. The blasting and heating is upward and the gas making downward.

The blow is generally divided into a dry blast followed by oil with blast.

The dry blast constitutes between 25 and 30% of the heating period. It consists in blowing air up through the checker brick for burning off the carbon deposited from the previous run.

The oil with blast follows the dry blast during which oil is introduced into the combustion chamber at the bottom of the generator. The hot gases from the combustion of the oil pass up through the checker bricks and store heat in them.

The run is divided into three periods:

1. Oil injection which constitutes about 64% of the run. In this period oil is introduced into the top of the generator with steam used for atomization. The steam and oil pass down through the hot checker brick; the oil gasifies and with the steam leaves the generator through the gas offtake connexion at the bottom and passes through the wash-box.
2. Standing purge which constitutes about 12% of the run. After shutting off the oil, steam continues to enter the generator through the oil sprays at the same rate at which it is used for atomization during the oil injection.
3. Scavenging purge which constitutes about 24% of the run. During this period the steam pressure on the oil sprays is increased or additional steam is passed through the generator from an auxiliary steam nozzle.

Two-shell Machine. The operating cycle with a two-shell Jones Machine may be 16–20 min. It is equally divided between the blow and run.

The blow consists of a dry blast and oil with blast.

The dry-blast period is between 40 and 45% of the blow. Primary air is introduced into the top of the primary generator and secondary air at the base of the secondary generator. The blast gases leave the machine through the stack valve at the top of the secondary generator.

During the oil with blast period, oil is introduced into the top of the primary generator. The hot gases from the combustion of the oil pass down through the primary generator, up through the secondary and out through the stack valve. If needed, secondary air is introduced at the base of the secondary generator.

The run is divided into three periods:

1. Tempering period, which amounts to about 5% of the run. Steam is introduced at the top of both the primary and secondary generators and at the base of the primary generator for cooling all sprays and burners.
2. Oil-injection period which is about 70% of the run. Oil is introduced through the make-oil sprays just above the primary and secondary make chambers. Steam is introduced at the top of the primary and secondary generators. It is superheated as it passes down through the superheaters located above the make chambers. The make-oil and superheated steam pass down through the make chambers in both generators where the oil is gasified. The gases leave the machine through the gas offtake connexion to the wash-box. If necessary, for cooling purposes, additional steam is introduced at the base of the primary generator.
3. Purge period is about 25% of the run. After the make-oil is shut off, the introduction of steam at the top of both generators continues. It is superheated in passing down through the superheaters and make chambers. While passing through the make chambers the superheated steam reacts with the carbon and coke deposited on the checker brick and forms blue gas.

With both single and two-shell machines steam is passed through all the oil sprays continuously as a cooling medium. The amount of steam is increased when oil is passed through the sprays in order to atomize the oil.

The following are normal temperature ranges of the refractory parts of the two types of machines:

	° F.
Single Shell:	
Arches	1,800–2,200
Middle checkers	1,800–2,000
Two-shell Jones:	
Primary superheater	1,900–2,100
Primary make chamber	1,650–1,750
Bottom of secondary generator	1,400–1,500
Secondary make chamber	1,550–1,650
Secondary superheater	1,350–1,450

The temperature of the gases at the gas offtake connexion may range from 1,400 to 1,600° F.

From the wash-box the gases pass through a series of scrubbers in which the tar, lampblack, and naphthalene are removed before entering a relief holder. From the relief holder the gas is pumped through purifiers in which hydrogen sulphide is removed, and then into a storage holder.

With a single-shell machine approximately 8·5 U.S. gal. of total oil is used per 1,000 cu. ft. of 550 B.Th.U. oil gas made. About 14% of the oil is used for heating and 86% for making. A two-shell machine uses about 7·5 U.S. gal. of total oil per 1,000 cu. ft., of which about 12% is used for heating and 88% for making.

The generators are generally equipped with base metal pyrometers, the thermocouples of which are located in the several chambers. Due to the high temperatures and the coating of the fire ends with carbon which acts as an insulating material, the value of pyrometers for temperature control is limited. The principal methods for temperature control are:

1. The inspection of the brickwork through sight cocks located at various points on the machine.
2. The appearance of the lampblack in the wash-box and scrubber overflows.
3. The temperature of the gas leaving the machine.

Gas produced.

The gas produced by the Pacific Coast oil-gas process is a mixture of blue gas and oil gas, the latter resulting from cracking oil at a high temperature. Most of the oil-gas operation is to produce a heating value of from 550 to 570 B.Th.U. per cu. ft. Such a gas contains approximately 25% blue gas and 75% oil gas. Carburetted blue gas of the same heating value contains approximately 80% blue gas and 20% oil gas.

The gas is very similar to coal gas made in coke ovens. The following are typical analyses of the oil gas made with a single and two-shell machine and coal gas made in a coke oven:

	Two-shell	*Single shell*	*Coke oven*
CO_2	4·85%	2·06%	1·5%
Ills.	3·67%	2·99%	4·1%
O_2	0·65%	0·57%	0·7%
CO	10·57%	8·44%	5·0%
H_2	49·35%	52·83%	52·4%
CH_4	25·40%	30·56%	28·3%
N_2	5 47%	2·56%	8·0%
B.Th.U. per cu. ft.	548	566	548
Sp. gr.	0·46	0·38	0·40

Depending upon the oil used and the heats carried, the oil gas leaving the wash-box contains from 150 to 350 grains of hydrogen sulphide per 100 cu. ft., 20 to 60 grains of organic sulphur, and 150 to 600 grains of naphthalene.

Reactions of Gas-making Period [19].

The reactions which take place during the gas-making period when steam and oil are simultaneously brought into contact with hot checker brick are very complex and, as in the case with the gasification of oil in the carburetted blue-gas process, many of them are unknown. The oils used are generally asphaltic base oils so that the hydrocarbons present are mainly of the naphthene and olefine series.

In addition to the reactions for the formation of hydrogen, hydrocarbons, and free carbon or lampblack, by decomposition of the oil, there are two classes of reactions in which steam takes part:

1. The coke residue from the distillation of the make-oil, and part of the carbon or lampblack formed by the decomposition of the oil, are deposited on the checker brick. Steam reacts with these carbon deposits, and forms blue gas. Steam may also react to some extent, to yield blue gas, with the lampblack formed in the cracking of the oil. Experiments [36, 1929] have indicated, however, that such a reaction between the steam and lampblack at temperatures up to 1,960° F. does not occur to any appreciable extent.
2. Steam may react directly with the hydrocarbons of the gas and oil vapours. The mechanism of these reactions has not been definitely fixed, but there is no doubt that carbon monoxide, carbon dioxide, and large amounts of free hydrogen are formed by them. It is possible that there may also be reactions between carbon dioxide and hydrocarbons of the gas and oil vapours with formation of carbon monoxide and more hydrogen.

Control of Carbon or Lampblack.

The carbon or lampblack formed by the decomposition of the make-oil, that is, not deposited on the checker brick, is carried out of the machine entrained in the gas. The carbon thus entrained with the gas is removed in the wash-box and scrubbers. The amount of this carbon recovered varies from 13 to 22 lb. per 1,000 cu. ft. of oil gas produced. More carbon is produced with a single-shell machine than with a two-shell machine.

The theoretical accumulation of carbon on the checker brick amounts to from 3·50 to 3·75 lb. per 1,000 cu. ft. of oil gas made. Some of this is blown out of the machine in the form of unburned carbon, and the balance remains to be burned out during stand-by periods, or partially used in making blue gas.

The best results in carbon control are obtained by making the greatest amount of blue gas, and by obtaining the greatest consumption of carbon during the blowing and heating period. A sacrifice in efficiency may be made by using excess air to accomplish this greatest carbon consumption, and the point where efficiency, carbon control, and smokeless stacks are obtained must be determined for each plant.

Using a better grade of oil, such as a distillate, gas oil will eliminate excessive carbon deposits on the checker brick. Such an oil is considerably more expensive than the residuum oil used in the oil-gas process.

The lampblack removed from the gas is usually processed to reduce the moisture content to about 50%. It is then burned under boilers simply as a means of disposal. One gas company briquettes the lampblack and sells it for domestic heating purposes.

New Process of Oil-gas Production [20]

L. B. Jones developed an improved oil-gas process in 1928 in which both the lampblack and the tar are converted into gas. This new process combines in one apparatus the following operations:

1. Cracking the oil in the presence of blue gas and superheated steam. This operation is similar to the carburetted blue-gas process.
2. Separating the lampblack physically by filtering the gas through a suitable filter bed.
3. Forming producer gas by blasting the lampblack with air, with or without steam, and using the producer gas instead of oil for heating the apparatus.
4. Converting the remaining lampblack into blue gas by treating with steam after bringing it to incandescence by the blasting, as outlined in no. 3, and using this blue gas and steam as the atmosphere for gasifying the oil.

Fig. 6 is a sketch of the apparatus. The generators are similar to a two-shell Jones Oil Gas Machine, except that both shells are the same height and each has a stack valve on the top. Each shell contains two sections of checker brick, one of which is a make chamber, while the other is a superheater. There is an oil spray just above the make chamber of each shell. Gas offtake connexions between the superheaters and the make chambers connect with the tops of two filter producers. Each filter producer has a gas offtake near the bottom, as well as steam and primary air inlets.

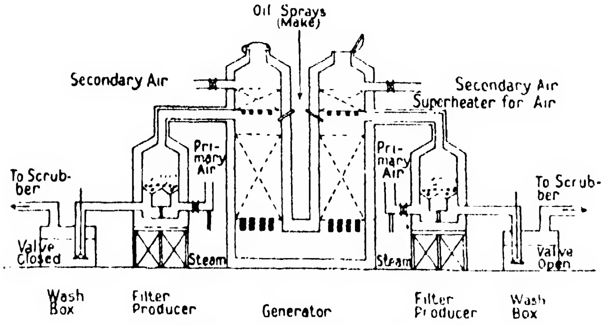


FIG. 6. Jones new process machine.

The filter producers contain a rotary ball grate, the details of which are shown in Fig. 7. The centre of the grate is rotated continuously, and since it is not truly conical, its rotation produces a slight wave motion as well as a rolling motion in the refractory spheres which rest upon it.

The gas offtakes of the filter producers are connected to two wash-boxes. A conical disk valve is used at the bottom of the dip-pipe in each wash-box.

Operation of Process.

With the left wash-box valve and stack valve of the left generator closed, primary air, with or without steam, is blown up through the left filter producer in which there is a layer of lampblack upon the refractory spheres. Producer gas is formed which passes over into the left generator. Secondary air enters the top of the left generator and passes down through the superheater. The producer gas and superheated secondary air meet. The hot products of combustion pass down through the left generator, up through the right generator, and leave through the stack valve at the top of the right generator. When the lampblack fuel bed in the left filter producer and the checker brick in the generators are heated to the proper temperature, the gas-making period is started.

The primary and secondary air valves on the left and the stack valve on the right are closed. Steam enters the left filter producer, passes up through the bed of incandescent lampblack, and forms blue gas. The blue gas and superheated undecomposed steam pass into the left generator, where they meet a spray of oil. The oil is cracked in an atmosphere of blue gas and steam by the hot checker brick of the make chambers in the two generators. The gases pass from the right generator into the top of the right filter producer, down through a layer of lampblack and the refractory spheres, and over through the wash-box. The temperature of the lampblack in the right filter producer is below the critical temperature for the decomposition of the oil gas, and acts as a mechanical filter. The lampblack suspended in the gas is deposited on this filter bed.

When the desired amount of oil has been introduced into the left generator, the make cycle is brought to an end. The left steam is turned off and the dip-pipe valves in the wash-boxes are reversed, the right being closed and the left opened. Steam and then primary air are introduced below the rotary grate of the right producer filter, purging the gas from the right filter producer and in turn from the right and left generators. The left stack valve is raised before any of the products of combustion have passed to the left filter producer and wash-box. Thus a new cycle proceeds from right to left.

The formation of oil gas in this process makes application of the principles previously discussed. The tar formed passes through the filter bed as vapours and is recovered in the condensing and scrubbing equipment. It resembles carburetted blue-gas tar.

The coke formed from the lampblack in the fuel bed is coarse and porous, with very little strength.

At the time the development of this process was completed, extensive natural gasfields were discovered in California. The spread of the use of natural gas led to the suspension of oil-gas operations in much of that territory. For that reason this process has not been used on a commercial scale on the Pacific Coast. The only commercial use of this process is at Honolulu, Hawaii, by the Honolulu Gas Company, Ltd. Operating results that have been obtained show a consumption of 6·072 total U.S. gallons of oil used per 1,000 cu. ft. of 518-B.Th.U. gas.

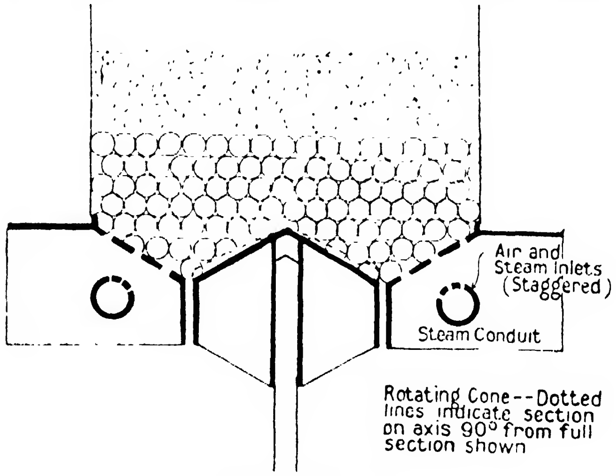


FIG. 7. Ball grate.

Dayton Oil-gas Process [21, 1921–35]

Dayton oil gas is a mixture of oil gas and producer gas made simultaneously.

In theory the process is very simple. Oil is atomized with a limited amount of preheated air into a hot retort or generator. The combustion of part of the oil furnishes heat to crack the rest of the oil into permanent gases.

Fig. 8 shows the improved Dayton generator. It consists primarily of a steel shell lined with refractory material. The reaction chamber is cylindrical in shape with a cone top. The preheated air and atomized oil are admitted through a heavy steel feed-tube that extends from the top of the generator to a point a few inches above its floor. No external heating is employed, the reaction being maintained by partial combustion of the oil.

The hot gas formed in the generator is withdrawn from the top through a horizontal heat exchanger in which the entering air is heated to about 700° F. The gas is cooled by a water spray in the top of the down-comer, and passes through a wash-box into scrubbers and finally into a holder. A stack valve is provided for venting the flue gases to the atmosphere during the heating period.

The heating value of the gas made is determined by the ratio of input air to oil. The greater this ratio, the higher is the reaction temperature and the lower the heating value of the gas. As the generator temperature increases from 1,350 to 1,650° F., the heating value decreases from 500 to 300 B.Th.U.

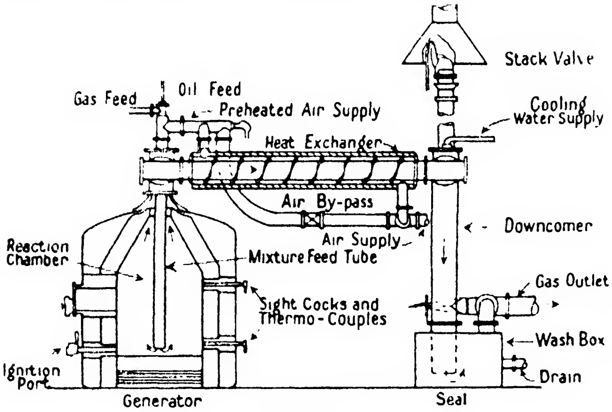


FIG. 8. Improved Dayton generator.

No lampblack is made in the Dayton process. The tar production varies with the reaction temperatures. It ranges from 8 to 20% of the oil used. The tar is very fluid and has a specific gravity of approximately 1.

The gas made requires no sulphur purification. Most of the sulphur in the oil is oxidized to water-soluble compounds, which are washed from the gas in wet scrubbers.

The oil used is a light fuel oil of from 33 to 38° API. gravity.

Table VII shows the oil requirements, gas analyses, and efficiencies of Dayton oil gas of various heating values.

TABLE VII

Oil Requirements, Efficiencies, and Analyses of Dayton Oil Gas of various Thermal Values

Amer. Gas Assoc. Proc. 1364 (1930)

B.Th.U. per cu. ft.	300	350	400	450	500
Generator temperature, ° F.	1,650	1,575	1,500	1,425	1,350
Gas analyses, % by volume:					
CO_2	3·60	4·60	5·40	5·90	6·10
Illuminants	6·60	9·20	12·00	14·50	15·90
O_2	0·50	0·50	0·50	0·50	0·50
CO	11·40	10·10	8·70	7·20	5·50
H_2	12·00	6·60	3·90	2·50	1·50
CH_4	10·80	8·60	7·60	7·60	8·70
N_2	55·10	60·40	61·90	61·80	61·80
Sp. gr.	0·85	0·94	1·00	1·02	1·03
Penn. light fuel oil:*					
U.S. gal. per 1,000 cu. ft.	2·67	3·15	3·65	4·10	4·62
Cu. ft. producer gas per U.S. gal.	264	252	210	184	160
Cu. ft. oil gas per U.S. gal.	110	78	64	60	56
B.Th.U. in gas per U.S. gal.	112,500	..	109,500	..	108,000
Efficiency, %	82	81	80	80	79
Average light fuel oil:†					
Gal. per 1,000 cu. ft.	2·68	3·20	3·81	4·60	..
Cu. ft. producer gas per U.S. gal.	264	236	200	164	..
Cu. ft. oil gas per U.S. gal.	110	76	61	53	..
B.Th.U. in gas per U.S. gal.	112,000	..	105,000	..	..
Efficiency, %	80	78	75	70	..
Tar, gal. per 1,000 cu. ft.	0·12	0·24	0·36	0·48	0·60

* Penn. light fuel oil, 38° API.—137,000 B.Th.U. per U.S. gal.
† Average light fuel oil, 38° API.—140,000 B.Th.U. per U.S. gal.

Its high specific gravity is largely the deterrent factor in the extensive use of Dayton oil gas by the manufactured-gas industry, particularly for mixing with any of the common types of manufactured gas.

Efficiencies of Various Gas Processes

The overall thermal efficiencies of the various gas-making processes are very high. They vary from 70 to 86%.

Coal Gas.

In 1926–7 heat-balance tests were made on four different types of coal-carbonization equipment. These tests were made by the Chemistry Department of the Massachusetts Institute of Technology under the direction of the Carbonization Committee of the American Gas Association. The period of each test was 30 days in which a uniform grade of coal was used. The types of carbonizing equipment tested were:

1. By-product coke oven.
2. Horizontal retorts.
3. Intermittent vertical retorts.
4. Continuous vertical retorts.

A summary of the results is as follows [8].

	By-product coke oven	*Horizontal retorts*	*Intermittent vertical retorts*	*Continuous vertical retorts*
Heat input:	%	%	%	%
In coke	11·25	9·37	12·09	10·93
In coal	88·07	89·33	86·93	87·72
In steam	..	.	0·07	0·89
Other items	0·68	1·30	0·91	0·46
Heat output	100·00	100·00	100·00	100·00
Coke made	55·70	56·20	56·30	55·62
Gas made	20·25	20·72	18·76	23·60
Tar made	5·87	5·81	5·70	6·97
Total for three major products	81·82	82·73	80·76	86·19
Miscellaneous:				
Cu. ft. of gas per lb. coal	5·66	6·06	5·67	7·15
B.Th.U. per cu. ft.	573	542	540	530
B.Th.U. per lb. coal	3,245	3,280	3,065	3,790
U.S. gal. dry tar per ton dry coal	12·40	11·60	11·40	14·60
Coke yield as % of coal carbonized	70·20	68·60	70·70	70·00
Ratio of heat output in form of coke, gas, and tar, and heat input in form of coal	92·90	92·62	92·90	98·26
B.Th.U. for carbonization per lb. coal, including credit for waste heat steam produced	1,320	1,420	1,485	985 1,127*
Lb. producer coke per ton coal carbonized	292	229	318	275
Lb. of steam from and at 212° F. per lb. producer fuel in waste heat boiler	0·59	1·14	1·96	5·74
Lb. ammonia (NH_3) per ton coal	6·36	4·92	5·94	3·38

* If steam to retort is included.

In fairness to the operation of the intermittent vertical retorts it should be stated that 75% of the retorts in the battery tested had been in operation about 8 years at the time of the tests, whereas the by-product coke ovens had been in operation 2 years, the horizontal retorts 4 years, and the continuous vertical retorts only a few months.

Carburetted Blue Gas.

No authentic heat-balance test has been made in the U.S.A. on a modern three-shell carburetted blue-gas machine. The following results, however, were obtained in an actual plant. Test 'A' was with regular gas oil, while tests 'B' and 'C' were with bunker oil with some reforming by passing it through the fuel bed. There was more reforming in Test 'C' than Test 'B'.

	Test 'A'	*Test 'B'*	*Test 'C'*
Input.			
1. Generator fuel, lb. per 1,000 cu. ft.	27·65	16·24	12·52
,, ,, B.Th.U. per lb.	11,680	13,100	13,100
2. Oil, U.S. gal. per 1,000 cu. ft.	2·98	4·51	4·22
,, B.Th.U. per U.S. gal.	145,800	150,800	151,400
3. Process steam, lb per 1,000 cu. ft.	51·80	25·80	20·20
,, ,, B.Th.U per lb.	1,129	1,129	1,129
Output			
1. Gas, B.Th U. per cu. ft.	530	536	529
2. Tar, U.S. gal. per 1,000 cu. ft.	0·70	1·37	0·78
,, B.Th.U. per U.S. gal.	143,500	161,000	170,500
3. Drip oil, U.S. gal. per 1,000 cu. ft.	0·03	..	0·04
,, B.Th.U. per U.S. gal.	138,000	.	120,500
4. Waste heat boiler steam.			
Lb. per 1,000 cu. ft.	18·00	18·00	18·00
B.Th U. per lb.	1,172	1,172	1,172
Heat balance, %			
Input:			
1. Generator fuel	39·50	23·10	19·90
2. Oil	53·30	73·80	77·30
3. Process steam	7·20	3·10	2·80
	100·00	100·00	100·00
Output, % of input:			
1. Gas	64·90	58·20	64·10
2. Tar	12·30	23·90	16·10
3. Dry oil	0·50	0·00	0·60
4. Waste heat boiler	2·60	2·30	2·50
Thermal efficiency	80·30	84·40	83·30

If bituminous coal is used for generator fuel, approximately 58% of the coal gas liberated is recovered in the finished gas and constitutes 8·44% of its heating value. This has very little effect on the thermal efficiency of the process as compared with coke as generator fuel. Any variation due to the use of bituminous coal is offset by a reduction in the amount of carburetting oil required.

Oil Gas—Pacific Coast Process.

In January 1920 the Railroad Commission of the State of California ordered an investigation of the production, transmission, distribution, and use of gas, and of such other matters pertaining to the gas service in California as appeared advisable. This was a joint investigation by the Railroad Commission and the gas companies, and included a study of the efficiency of the Pacific Coast Oil Gas Process with single-shell machines as well as two-shell machines. The final report was issued 3 May 1924 [7].

The following thermal efficiencies were obtained when making a 550-B.Th.U. gas with different sizes and types of oil-gas machines:

	Two-shell		*Single-shell*		
Size diameter	12 ft.	18 ft. 9 in.	14 ft.	20 ft.	22 ft.
Heat input:	%	%	%	%	%
Heating value of make oil	84·1	84·1	85·5	89·2	86·0
,, ,, heat oil	12·0	11·4	11·8	8·0	11·7
Heat in steam used	3·4	4·0	2·2	2·3	1·7
Miscellaneous	0·5	0·5	0·5	0·5	0·6
	100·0	100·0	100·0	100·0	100·0
Heat recovered:					
Heating value of gas	48·0	48·4	42·9	45·8	43·0
,, ,, lampblack	17·0	15·8	24·8	23·6	24·5
,, ,, tar	6·1	5·8	2·8	1·9	1·7
Total heat recovered	71·1	70·0	70·5	71·3	69·2

Refinery Oil Gas.

Based upon data in a paper entitled 'The Refinery Gas Reforming Plant at Chester, Pa.', in the 1930 *Proceedings of the American Gas Association*, p. 1471, the following results were obtained when producing a 520-B.Th.U. gas:

Fuel per 1,000 cu. ft.	11·87 lb.
Oil gas per 1,000 cu. ft. (1,575 B.Th.U.)	259 cu. ft.
Tar produced per 1,000 cu. ft.	0·06 U.S. gal.

Based upon 13,500 B.Th.U. per lb. of generator fuel and 150,000 B.Th.U. per U.S. gal. of tar, a calculated heat balance shows that of the heat input:

91·0% is recovered as gas
1·6% ,, ,, tar
92·6% thermal efficiency

High-heating Value Gas

When natural gas replaces manufactured gas (about 550 B.Th.U.) it is necessary to change the adjustments of all the gas appliances. While this change is primarily due to the higher heating value of the natural gas, it is also due to the burning characteristics of the constituents of natural gas. It does not follow, as one might readily suppose, that a manufactured gas having the same heating value as natural gas can be substituted for or mixed with natural gas and render satisfactory service.

The extensive replacement of manufactured gas by natural gas has resulted in the development of processes and methods for making a manufactured gas of high heating value which can be used to augment the supply of natural gas at times of peak loads or as a complete substitute for natural gas in the event of an interruption in the supply due to a break in the natural-gas transmission line or to some other cause.

The manufactured gases which are the best substitutes for natural gas are straight oil gas or oil gas mixed with a small percentage of blue gas. These gases can be made with the equipment used for the manufacture of carburetted blue gas and Pacific Coast oil gas. This equipment can produce such a gas at the same therm rate (therm—100,000 B.Th.U.) at which gases of lower heating value are produced.

Refractory Screen Oil-gas Process [12, 1932–3]

This process was developed by the Combustion Utilities Corporation, New York, N.Y., in 1932. It can be used with a standard three-shell carburetted blue-gas machine with a few modifications.

Equipment.

Fig. 9 is a diagrammatic drawing of a three-shell carburetted blue-gas machine equipped for the Refractory Screen Oil-gas Process. The changes required are:

1. Generator grates are substituted by checkerwork refractory on which a bed is built of small non-spalling high-temperature resistant refractory blocks. This constitutes the so-called refractory screen.
2. A water-cooled oil spray is inserted through the generator-charging door, or the door is removed and a steel cover plate supporting the oil spray is bolted in place.
3. An additional air nozzle is provided for the down blasting of the refractory bed.
4. A gas connexion and hot valve is required between the generator bottom and the carburettor top.
5. Oil burners are provided in generator and carburettor for heating purposes.

has the consistency of coal tar made in by-product coke ovens. Its specific gravity is about 1·13.

While no lampblack is perceptible in the wash-box or scrubber overflows, undoubtedly some is formed. It is probably recovered as free carbon in the tar.

Table IX shows typical operating results when producing an oil gas of approximately 1,000 B.Th.U. by the Diesel Oil-gas Process.

Production of Oil Gas in a Carburetted Blue-gas Machine [24, 1933–5]

Considerable work has been done in the past 4 years on the production of 800 to 1,000 B.Th.U. gas in a standard three-shell carburetted blue-gas machine using various modifications of standard carburetted blue-gas operating procedure.

A blower is used for heating the checker brick in the carburettor and superheater similar to the carburetted blue-gas process. Since very little or no blue gas is made, steam along with air is passed through the fuel bed in the generator. The use of steam in this manner is to prevent excessive heating of the generator and excessive formation of clinker.

During the run or make period oil gas is mostly made by introducing oil into the top of the carburettor. It is gasified by passing through the hot checker brick in the carburettor and superheater. After the proper amount of oil has been introduced, the oil gas is purged from the machine with either steam or blue gas.

E. L. Fischer has made high B.Th.U. gases in a standard carburetted blue-gas machine by the following methods:

a. Crack oil in carburettor at temperature just under lampblack formation. Mix with resulting oil gas sufficient blue gas to obtain required B.Th.U.

b. Crack oil in carburettor in steam atmosphere, using sufficient temperature to produce B.Th.U. desired.

c. Crack oil in carburettor at temperature just under lampblack formation as in (*a*), also crack sufficient oil through generator fire to bring B.Th.U. to desired value.

d. Operate as in (*c*) to produce about 750-B.Th.U. gas, then mix with sufficient uncracked butane to produce desired B.Th.U.

e. Operate as in (*a*), using butane in carburettor instead of oil.

If the oil is cracked to produce an oil gas of less than 900 B.Th.U. per cu. ft., considerable lampblack is formed. A heavy pitch-like tar is also formed. Due to the formation of lampblack and tar considerable operating difficulties are encountered.

The Mechanism of Cracking.

The controlling factors in the production of high-heating value gas are:

1. The B.Th.U. per cu. ft. This should not vary more than plus or minus 5%.
2. The specific gravity. This should not vary more than plus or minus 10%.
3. The proportions of fast and slow burning constituents in the gas.

A uniform cracking temperature is essential. Usually a variation of 25 or 50° F. in the cracking temperature will cause an appreciable variation in all three factors.

An oil gas made in a carburetted blue-gas machine or by the refractory screen oil-gas process or the Diesel oil-gas process contains a small amount of blue gas. Such an oil gas of any given heating value has a fairly definite specific gravity and composition. During the tests made at San Rafael in May 1932 [10] analyses were made of oil gases whose heating value varied considerably. A chart was prepared from these analyses in which the specific gravity, unsaturated hydrocarbons, saturated hydrocarbons, and hydrogen were plotted against the heating value. According to this chart the changes in the character and composition of the oil gas varied as follows with the heating value:

Heating value B.Th.U. per cu. ft.	*Sp. gr.*	*Unsaturated hydrocarbons*	*Saturated hydrocarbons*	*Hydrogen*
		%	%	%
700	0·48	10	35	43
800	0·54	14	41	34
900	0·61	19	45	26
1,000	0·67	23	47	20
1,100	0·73	27	46	14

Production of Light Oils or Motor Fuels

One of the principal sources of benzol and toluol during the World War, 1914–18, was carburetted blue gas. Light oil vapours in the gas were removed by scrubbing with a straw oil. The light oils recovered in this manner amounted to approximately 10% of the carburetting oil used. The composition of these crude light oils was as follows:

Benzol	42%
Toluol	25%
Solvent naphtha, wash oil, naphthalene, &c. . .	33%

When the maximum carburetting efficiency was obtained, these oils contained less than 2% paraffin compounds.

Removing the light-oil vapours from carburetted blue gas reduces the heating value from 4 to 8%. This means that in order to produce a gas of a given heating value, more carburetting oil is required if the light-oil vapours are recovered than would be needed if they remain in the gas. Partly for this reason, but principally because the light oils yield more revenue when sold as gas than as motor fuel, gas companies, as a rule, do not remove light oils from the gas. One gas company on the Pacific Coast making 550-B.Th.U. oil gas by the Pacific Coast oil-gas process recovers the light oils from the gas and sells them for motor fuel. The oil-gas sets are operated considerably below their rated capacity in order to produce a maximum amount of light oils. The light oils thus produced contain an appreciable amount of paraffin compounds. These are not objectionable if the light oils are used as motor fuel. If benzol and toluol are recovered for nitrating purposes, the presence of paraffin compounds—in excess of 2%—is objectionable.

About 15 years ago the author (Willien) had some experience with the production of blaugas. This was a liquefied oil gas. It was made by gasifying a distillate gas oil in horizontal fireclay retorts, similar to the retorts used for carbonizing coal. The oil was gasified at a temperature of about 1,000° F. Approximately 40 cu. ft. oil gas of the following composition was produced per gallon of oil:

CO_2	*Ills.*	O_2	CO	CH_4	H_2	N_2
1·0	43·8	0·8	1·8	30·5	18·9	3·2

About 50% of the gas oil used was recovered as tar oil. A distillation test on this tar oil showed 43·7% distilling below 200° C. The distillate lost 15% on washing with sulphuric acid and had a gravity of 45° Bé. Fig. 10 shows a comparison of a distillation curve on this distillate with three commercial gasolines on the market at that time. One of these gasolines was known to be blended with 30–5% benzol. Fig. 11 shows the distillation curve on the original gas oil and the residue from the tar oil after distilling the fraction up to 200° C.

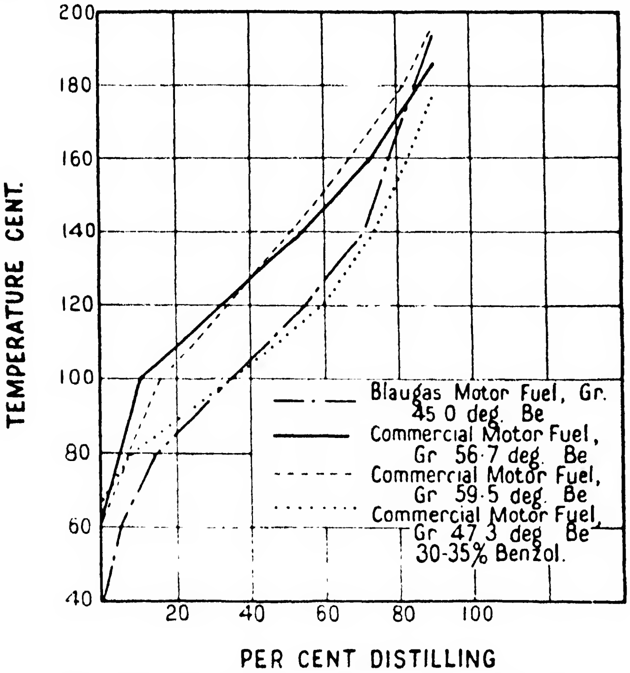


FIG. 10. Distillation curves on blaugas motor fuel and commercial motor fuels.

It is interesting to note that the distillation curve on the motor-fuel fraction from the tar oil is practically the same as the curve for the commercial gasoline blended with benzol.

The curves in Fig. 11 indicate that the residue from the tar oil after removing the motor fraction is as suitable for processing in the retorts as the original oil.

By removing the light oils from the oil gas an additional one-tenth of a gallon of motor fuel should be recovered. Allowing a 15% washing loss, the total motor fuel recovered per gallon of gas oil would be 27%. Assuming that the residue tar oil yields the same amount of products on a second processing as the original gas oil, a gallon of gas oil should yield 35% motor fuel and 51 cu. ft. of oil gas.

Similar results should be obtained by cracking at a low temperature in a carburetted blue-gas machine. Since most gas companies have idle generating equipment during the summer months, it should be possible through some sort of co-operative arrangement between the oil and the gas companies to use this idle equipment for producing motor fuel, the gas companies keeping the gas and the oil companies supplying the gas oil and taking the motor fuel.

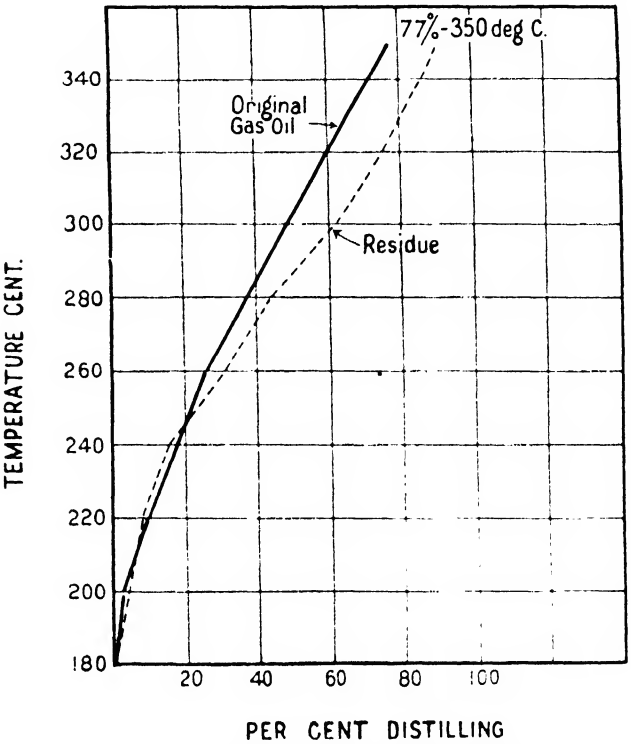


FIG. 11. Distillation curves on gas oil before and after cracking.

REFERENCES

1. American Gas Association. *Gas Chemists' Handbook*, 1929, 60–2.
2. BROWNLEE, R. H. *Chem. and Met. Eng.* **34**, 737–41 (1924).
3. DICK, I. B. *Amer. Gas J.* 32 (June 1933).
4. DOWNING, R. C., and POHLMANN, E. F. *Proc. Amer. Gas Assoc.* part I, 588 (1916).
5. FERGUSON, H. E. Private communication to Morgan, author of reference 13.
6. Final Report of Investigation made by the Joint Committee on Efficiency and Economy of Gas of the Railroad Commission of the State of California. Issued 3 May 1924, p. 96.
7. Final Report of Investigation made by the Joint Committee on Efficiency and Economy of Gas of the Railroad Commission of California. Issued 3 May 1924.
8. *Gas Engineers' Handbook*, 1st ed., Table 100, p. 397. (Published by McGraw-Hill Book Co., Inc., New York.)
9. HARPER, R. B. *Amer. Gas Eng. J.* 312 (12 April 1919).
10. HARRITT, J. A., WILLS, FRANK, and WILLIEN, LEON J. *Proc. Pacific Coast Gas Assoc.* (1932). *Western Gas* (Aug. 1932).
11. —— —— —— *Proc. Pacific Coast Gas Assoc.* 262 (1932), and 93 (1933). *Western Gas* (Aug. 1932).
12. JOHNSTON, ALFRED. *Proc. Amer. Gas Assoc.* 892 (1932). Also *Gas Age-Record* (18 June 1932, 27 May 1933). *Amer. Gas J.* (Aug. 1933).
13. MORGAN. *American Gas Practice*, 2nd ed., **1**, 459.
14. MORGAN. *American Gas Practice*, 2nd ed., **1**, 460.
15. —— *American Gas Practice*, 2nd ed., **1**, 463.
16. —— *American Gas Practice*, 2nd ed., **1**, 467.
17. —— *American Gas Practice*, 2nd ed., **1**, 475.
18. —— *American Gas Practice*, 2nd ed., **1**, 480.
19. —— *American Gas Practice*, 2nd ed., **1**, 582.
20. —— *American Gas Practice*, 2nd ed., **1**, 609.

JONES, L. B. *Western Gas* (Dec. 1929). Also, *Proc. Pacific Coast Gas Assoc.* 602 (1929).

JONES and HARRITT. *Proc. Amer. Gas Assoc.* 1349 (1930).

21. —— *American Gas Practice*, 2nd ed., **1**, 617.

U.S.P. 1,506,164 (26 Aug. 1924).

BINNALL, F. C. *Ind. Eng. Chem.* **13**, 242 (1921).

FERGUSON, H. E. *Proc. Amer. Gas Assoc.* 1361 (1930). *Gas Age-Record*, **65**, 849 (1935).

HASLAM and RUSSELL. *Fuels and Their Combustion*, 644 (McGraw-Hill Book Co., New York, 1926).

22. MURDOCK, W. J. *Proc. Amer. Gas Assoc.* 924 (1926).
23. MURPHY, E. J. *Gas Age-Record*, **65**, 389 (1930).
24. PETTYJOHN, E. S. *Amer. Gas Assoc. Monthly* (Aug. 1933). *Proc. Amer. Gas Assoc.* (1933).

DIETERLE, E. A. *Proc. Amer. Gas Assoc.* 806 (1933).

YOUNG, H. B. *Proc. Amer. Gas Assoc.* 795 (1933).

NAGLER, K. B. *Proc. Amer. Gas Assoc.* (1933).

Sedgwick, D. L., Steinwedell, W. E., Carson, H. J., and Fischer, E. L. *Proc. Amer. Gas Assoc.* (1933).

Willien, Leon J. *Gas Age-Record* (4 Nov. 1933).

Young, H. B., and Workman, D. M. High B.Th.U. Amer. Gas Assoc. Joint Committee Conference of the Production and Chemical Committees, 21–2 May 1934.

Beard, W. K. Amer. Gas Assoc. Joint Committee Conference of the Production and Chemical Committees, 13, 14, 15 May 1935.

Fischer, E. L. Amer. Gas Assoc. Joint Committee Conference of Production and Chemical Committees, 13, 14, 15 May 1935.

25. Pexton, S. *Gas J.* 594 (London, 27 Nov. 1929).

26. Pohlmann, E. F. *Proc. Amer. Gas Assoc.* 1193 (1930).

Ferguson, H. E. *Gas Age-Record*, 235 (24 Aug. 1929).

27. Private communication to the author (Willien), 1925.

28. Report of Sub-Committee on Uniform Oil Efficiency. *Proc. Amer. Gas Assoc.* 911 (1926), and 1053 (1927).

29. Report of Sub-Committee on Refinery Oil Gas. *Proc. Amer. Gas Assoc.* 1465 (1930).

Schlegel, C. A. *Proc. Amer. Gas Assoc.* 1466 (1930).

Rincliffe, R. G. *Proc. Amer. Gas Assoc.* 1471 (1930).

Terzian, H. G. *Proc. Amer. Gas Assoc.* 1167 (1931).

30. Richards, J. V. *Proc. Amer. Gas Assoc.* 1329 (1930). *Gas Age-Record*, 809 (31 May 1930)

Dashiell, P. T. *Proc. Amer. Gas Assoc.* 886 (1930). *Gas Age-Record*, 223 (14 Feb. 1931). *Proc. New England Gas Assoc.* (1931).

Stewart, W. D. *Proc. Amer. Gas Assoc.* 813 (1924). *Proc. Amer. Gas Assoc.* 1222 (1925).

Davis, R. F. 1931 Joint Production and Chemical Conference of Amer. Gas Assoc.

Harvey, W. J. 1931 Joint Production and Chemical Conference of Amer. Gas Assoc.

Parke, F. B. *Proc. Amer. Gas Assoc.* 897 (1934).

31. Vittinghoff. *Proc. Amer. Gas Assoc.* 1086 (1927).

Mighill, T. A. *Proc. Amer. Gas Assoc.* 1093 (1927).

Griffith, R. H. *J.S.C.I.* (1928, also 1929). *Proc. Amer. Gas Assoc.* 1189 (1930).

32. Whitaker, M. C., and Leslie, E. H. *Ind. Eng. Chem.* 593 (July 1916).

33. White, Prof. A. H., and Merkus, P. J. *Proc. Amer. Gas Assoc.* 986 (1934).

34. Willien, Leon J. *Gas Age-Record*, 603 (25 Apr. 1925), and 663 (7 Nov. 1925).

35. —— *Proc. Amer. Gas Assoc.* 966 (1934).

36. —— *Proc. Pacific Coast Gas Assoc.* 556 (1929).

37. Willien and Stein. *Proc. Amer. Gas Assoc.* 1036 (1927).

Evans, O. B. *Proc. Amer. Gas Assoc.* 1219 (1929).

Hall, E. L. *Proc. Amer. Gas Assoc.* (1930).

Willien, Leon J. *Proc. Amer. Gas. Assoc.* 1221, 1223 (1929). *Gas Age-Record*, **64**, 717 (1929).

Stein, Louis. *Proc. Amer. Gas Assoc.* 1490 (1930).

THE EVALUATION OF OILS FOR GAS MAKING—ENGLISH PRACTICE

By **R. H. GRIFFITH, D.Phil.**

The Gas Light and Coke Company

IN English gas-making practice, gas oil is cracked for the purpose of enriching water gas to raise its calorific value. The cracking process is carried out in a carburettor and superheater, attached to the water-gas generator, which are filled with a checker-work of refractory bricks and are heated during the blow period of the gas-making cycle to about 750° C. The yield of gas from the oil depends on (1) the temperature of the cracking vessels, (2) the rate at which the oil is injected, and (3) the composition of the oil used. Methods for the valuation of gas oils, which do not depend on actual cracking experiments, are based on the chemical and physical properties of the hydrocarbon.

Ross and Leather [7, 1902] used the refractive index, specific gravity, and behaviour towards bromine as criteria for the value of an oil, and concluded that paraffin hydrocarbons were the most desirable. Many other investigators subsequently carried out small-scale experiments with oils of different types but did not give sufficient attention to control of the other variables mentioned above to enable them to find any closer relation between chemical constitution and value for gas making. Satisfactory methods for the analysis of hydrocarbon mixtures were also not available at the time.

A wide range of oils was later investigated by Griffith [2, 1929], the samples being analysed with reference to unsaturated, aromatic, naphthene, and paraffin hydrocarbons (see Appendix), and the maximum obtainable gas yield being determined for each oil by a number of experiments. It was found that a direct relation exists between the content of open-chain hydrocarbons (unsaturated and paraffin together) and the thermal yield of permanent gas. This method of expressing the efficiency of oil-cracking proved particularly convenient in view of the adoption of the calorific value standard in the gas industry. In Table I are given the results obtained by cracking oils of widely varying composition in an experimental furnace supplied with a stream of hydrogen. It is clear that the thermal yield follows closely the figures in column 2, which are based on analysis of the hydrocarbons. The sum of the percentage of paraffin and unsaturated hydrocarbons present in a gas oil has therefore been chosen as its valuation number. Examination of the oil by this analytical method has the advantage of being simple and rapid; it has also been found capable of giving results in close agreement when determinations are carried out by different manipulators in separate laboratories.

Later investigators have suggested alternative methods of analysis, but are in agreement as to the value of paraffin hydrocarbons and the desirability of having as low a content of aromatic compounds as possible. Van Dijk [9, 1933], for example, advocates the analytical method of Waterman, while Schläpfer and Schaffhauser [8, 1933] again point out that efficiency of cracking of an oil will depend on the temperature and rate at which it is decomposed. In view of the influence of hydrogen on the reactions involved, it is of interest to record the composition of the gases [3, 1934] produced from two carburetted water-gas plants under various conditions, as shown in Table II.

TABLE I

Oil no.	*Sum of paraffins and unsaturateds*	*Max. therms per gal.*
8A	81·7	1·45
24	75·5	1·34
14	72·8	1·32
4	70·3	1·31
11	70·1	1·30
12	68·4	1·28
20	67·6	1·31
1	66·8	1·28
13	66·5	1·24
6	65·5	1·29
34	64·1	1·28
9	63·9	1·17
7	62·0	1·27
8	61·9	1·27
17	61·9	1·18
22	61·4	1·22
2	60·1	1·20
3	59·5	1·19
32	59·5	1·13
10	59·1	1·20
23	56·2	1·17
5	49·9	1·18
43	47·4	1·06
45	47·2	1·04
19	45·6	1·16
40	39·9	1·02
30	38·8	1·08
16	32·3	0·85
36	25·6	0·96
48	18·5	0·72
15	28·4*	0·50

* Including naphthenes.

These results emphasize the importance of control of temperature and rate of oil feed in any attempt to evaluate different types of oil by actual cracking experiments, and failure to observe these precautions has undoubtedly led to confusing statements from time to time. The conclusions of Murphy [6, 1930] that naphthenes have a relatively high carburetting value are based on a limited series of experiments, and other cases where cyclohexane has been chosen as representative of this class of hydrocarbon are similarly open to objection. The data on which Table I is based show clearly that cyclic components are undesirable [2, 1929] but do not attempt to decide whether naphthenes are actually superior to aromatic hydrocarbons. That the valuation method outlined above is applicable to works' practice is indicated by data from Domisse [1, 1933], who also provides an extensive bibliography of the subject.

As the efficiencies are expressed on the basis of gaseous therms per gallon of oil, it is to be expected that the boiling-point range of the oil will have some small influence on the results. This is actually found to be the case for two different reasons: (1) that there is greater weight of fuel per gallon of the high-boiling oil, so that within certain limits set by the ease of vaporization in the cracking vessels there is a larger yield of gas; and (2) that paraffin

TABLE II

Test no.	Cracking temp., °C.	Gal. oil per 1,000 cu. ft.	Gal. oil per min.	Cu. ft. gas formed from 1 gal. oil	Therms per gal.	Cubic feet*		
						CH_4	C_nH_m	H_2 per gal. absorbed
Plant A 1	805	1·92	5·5	65·7	1·259	60·4	35·9	30·7
2	810	1·83	5·0	67·7	1·269	61·2	37·1	31·1
3	805	2·01	6·0	66·6	1·237	59·2	37·3	34·8
4	810	1·62	4·5	68·5	1·334	61·7	43·8	37·0
5	760	2·04	5·5	56·4	1·202	48·5	39·2	31·4
6	715	1·96	(5·5)	51·4	1·220	45·9	35·7	30·1
7	805	1·82	3·7	68·7	1·369	64·3	42·3	37·9
8	805	1·87	7·3	53·1	1·157	52·9	32·6	32·6
9	860	1·84	3·7	54·9	1·217	59·2	31·5	35·9
Plant B 1	(585)†	1·26	1·5	51·9	1·13	57·3	32·6	38·0
2	,,	0·43	0·5	- 16·3	0·94	74·4	44·2	130·0
4	,,	0·93	2·0	12·9	1·10	36·9	27·0	51·8
5	,,	0·45	0·25	17·9	0·99	64·9	40·3	87·3
6	,,	1·28	0·75	43·7	1·05	46·9	19·5	22·7

* C_nH_m indicates olefine hydrocarbons.

† This temperature is at superheater outlet.

hydrocarbons of boiling-point about 200–250° C. are appreciably more stable than those of higher boiling-point, so that they do not decompose so rapidly (cf. Holmes [5, 1932]). Allowance for boiling-point is included in a formula of Schläpfer [8, 1933], where the evaluation factor is equal to KH/G; K being the average boiling-point of the oil under 10 mm. pressure, H the hydrogen content, and G the specific gravity.

The recent introduction of cetene values for Diesel fuels suggests that such a number would give a fair approximation to the gas-oil valuation number. It is evident that the properties required for a good gas oil are rather similar to those necessary in a fuel for a compression-ignition engine, but on account of some differences in the behaviour of naphthene and unsaturated hydrocarbons in the two cases it still appears preferable to employ separate standards.

The chemical composition of the gas oil has little effect on that of the tar produced by the carburetted water-gas plant, but the volume of tar increases rapidly as the valuation number decreases; this is a consequence of the greater stability of the cyclic hydrocarbons.

APPENDIX

Analysis of Gas Oils for Evaluation

For full experimental details of the method adopted for the analysis of gas oils, reference should be made to the original publications [2, 1928; 4, 1933].

Distillation. 200 ml. of the oil are distilled from a standard 250-ml. Jena flask and the distillation curve constructed from the temperature/per cent. distillate readings. From this the mean boiling-point (T° C.)—the temperature at which 50% of the oil has distilled—is found.

Unsaturated Hydrocarbons. 50 ml. of the total distillate obtained previously are shaken with 100 ml. of 80% sulphuric acid for 15 minutes. After settling for 2 hours, the oil layer is separated, washed with water, alkali, and water again. The oil is then drained into a 100-ml. Jena flask and distilled to the end-point reached in the first distillation. The diminution in volume represents the unsaturated hydrocarbons present.

Aromatic Hydrocarbons. 20 ml. of the unsaturated free oil are shaken for 15 minutes with 50 ml. of sulphuric acid (98%). The volume of oil separating after standing for 2 hours is measured, the diminution being due to removal of aromatic hydrocarbons.

Naphthenes. The aniline point of the oil, carefully separated from the acid in the previous stage, is determined. 5 ml. each of oil and dry redistilled aniline are heated in a jacketed test-tube till miscible, the temperature (° C.) at which a cloud first appears upon cooling being taken as the aniline point.

The aniline point of a mixture of paraffin hydrocarbons of mean boiling-point T° C. may be obtained by interpolation from the following table:

B.pt. T° C.	Aniline-point
180	76·3
200	79·1
220	82·0
240	85·0
260	88·3
280	90·9
300	93·7
320	96·9
340	99·5
360	101·3

The observed aniline point is subtracted from this value, and the difference, multiplied by 0·4, gives the percentage of naphthenes present in the final paraffin-naphthene mixture.

Paraffin Hydrocarbons. The percentage of paraffin hydrocarbons in the original oil is then calculated by difference, knowing the relative amounts of unsaturated, aromatic, and naphthene hydrocarbons.

REFERENCES

1. Domisse. *Het Gas*, **53**, 42 (1933).
2. Griffith, R. H. *J.S.C.I.* **48**, 252 T (1929); **47**, 21 T (1928).
3. —— *Water Gas*, 96 (Benn, London, 1934).
4. Griffith, R. H., and Hollings, H. *J.I.P.T.* **19**, 701 (1933).
5. Holmes. *Gas J.* **199**, 459, 505 (1932).
6. Murphy. *Proc. Amer. Gas. Assoc.* **12**, 1189 (1930).
7. Ross, R., and Leather, J. P. *J.S.C.I.* **21**, 676 (1902); *Analyst*, **31**, 284 (1906); **32**, 241 (1907).
8. Schläpfer and Schaffhauser. *Monatsbull. Schweiz. Ver. Gas- u. Wasserfachm.* **13**, 125, 159, 193 (1933).
9. Van Dijk. *Het Gas*, **53**, 449 (1933).

OIL FUEL

THE INDUSTRIAL APPLICATION OF FUEL OILS, INCLUDING BURNER PRACTICE

By I. LUBBOCK, M.A., A.M.I.Mech.E., F. J. BATTERSHILL, and R. H. B. FORSTER, B.Sc.

I. COMBUSTION

1. Outline of Principles

OIL has been found to be a very satisfactory fuel for a large number of heating operations. The measure of success obtained depends, however, on a number of fundamental considerations. There are three essential factors:

(1) A suitable appliance for burning the oil. This includes the supply of the fuel and the combustion air at the correct pressure and velocity with provision for correct mixing.
(2) A combustion chamber of the right shape and dimensions.
(3) A correctly designed furnace or heat-transferring appliance. This involves consideration of the working temperature and of the quantity of heat to be generated or transmitted.

It is proposed to deal only with those elementary principles of combustion of oil fuel which, taken in conjunction with these three groups, form the basis of most of the practical work carried out.

The properties of oil fuels of different grades and from different sources vary considerably. An average specification of a typical light fuel oil would be as follows:

Specific gravity at 60° F.	0·92
Viscosity, Redwood No. 1, at 100° F.	200 sec.
Calorific value (gross)	19,000 B.Th.U. per lb.
Flash-point (closed)	190° F.
Analysis:	
Carbon	87·4%
Hydrogen	11·0%
Sulphur	1·45%
Oxygen	0·15%

On the above analysis the air required theoretically for complete combustion is approximately 14 lb. per lb. of oil, and the maximum possible percentage of CO_2 in the dry gaseous products of combustion is 15·9.

On the other hand, a typical gas oil, taken at random, would have the following properties:

Specific gravity at 60° F.	0·86
Viscosity, Redwood No. 1, at 100° F.	35 sec.
Calorific value (gross)	19,500 B.Th.U. per lb.
Flash-point (closed)	180° F.
Analysis:	
Carbon	85·5%
Hydrogen	13·6%
Sulphur	0·4%
Oxygen	0·5%

In this case approximately 14·7 lb. of air would be required theoretically per lb. of oil, and the maximum possible CO_2 percentage would be 15·05.

From an examination of the analyses of a large number of oils it appears that the air required theoretically per lb. of oil lies roughly within the range of 14 to 15 lb. As a basis of calculation for average conditions it is usual to allow 30% excess air, although naturally it is possible to obtain variations from almost the theoretical minimum of air up to several hundred per cent. excess, according to conditions or requirements.

The chief factors governing the attainment of low excess air are good oil atomization combined with correct air control design so as to give the maximum possible turbulence. Highly preheated air appears to help in this connexion, but only if the other conditions are correct.

From the point of view of economy it is essential to keep the percentage of excess air at a minimum. This is particularly important in the case of furnaces operating at high temperatures. The losses due to excess air can be read off readily from the chart represented by Fig. 1.

Taking for example a furnace in which the heat required in the working chamber is 100,000 B.Th.U. per hour for useful work and radiation, and assuming that the temperature at which the gases leave the furnace is 2,000° F., two cases will be examined to show the effects of excess air, i.e.

(*a*) with 30% excess air.
(*b*) with 100% excess air.

(*a*) Referring to Fig. 1, the heat carried out in the waste gases is 11,200 B.Th.U. per lb. of oil burnt, leaving a useful value of (19,000 − 11,200), i.e. 7,800 B.Th.U. per lb. This value is indicated on the right-hand scale. In this case the oil consumption would therefore be 100,000 ÷ 7,800 = 12·8 lb. per hour.

(*b*) With 100% excess air the useful heat equals 2,500 B.Th.U. per lb., and in this case the oil consumption becomes 100,000 ÷ 2,500 = 40 lb. per hour.

This chart also affords a means of determining the theoretical flame temperature which can be found at the intersection of the diagonal line with the top horizontal scale.

All calculations involved have been based on the following ultimate analysis of the oil:

Carbon	86·6%
Hydrogen	12·4%
Oxygen	0·5%
Sulphur	0·5%

The specific heat of hydrogen has been taken according to Partington and Shilling, while for all other gases the equations proposed by Goodenough and Felbeck have been used. These are all given in Spiers, *Technical Data on Fuel* [8].

The actual flame temperature can be deduced by calculating the heat introduced in the combustion air and the heat lost by radiation from the flame.

In connexion with the subject of flame temperature dissociation of the combustion products has a negligible effect at temperatures below 3,100° F. Fig. 2 indicates the reduction in theoretical flame temperature due to this cause.

The dissociation calculations are based on the charts prepared by A. V. S. Underwood which are reproduced in Spiers, *Technical Data on Fuel* [8]. The results have been checked by the information given in *Fuels and Their Combustion* [3] by Haslam and Russell.

2. Oil-burning Appliances

The appliances used for burning oil fuel can be divided broadly into the two following classes:

(*a*) Vaporizing burners.
(*b*) Atomizing burners.

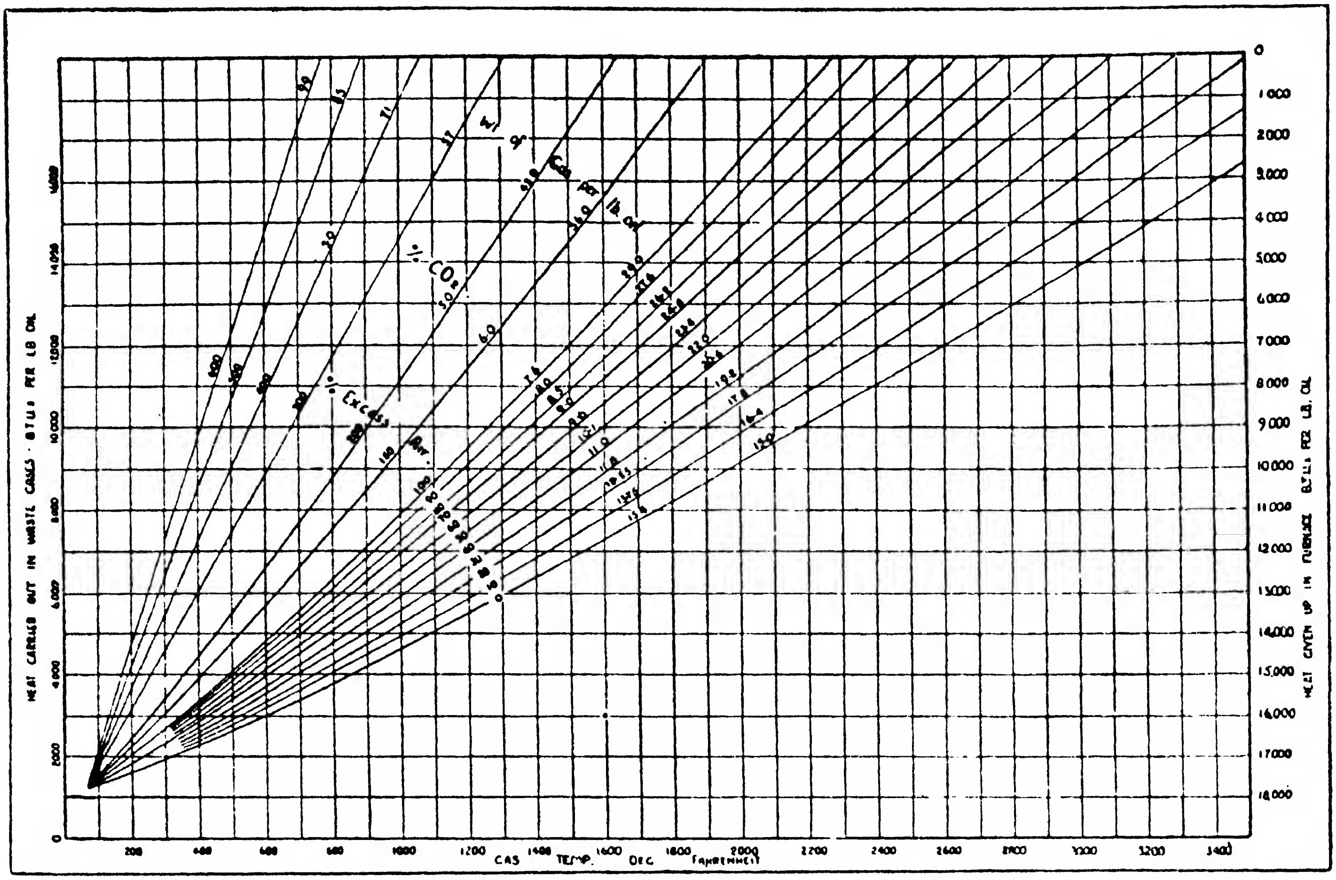


FIG. 1.

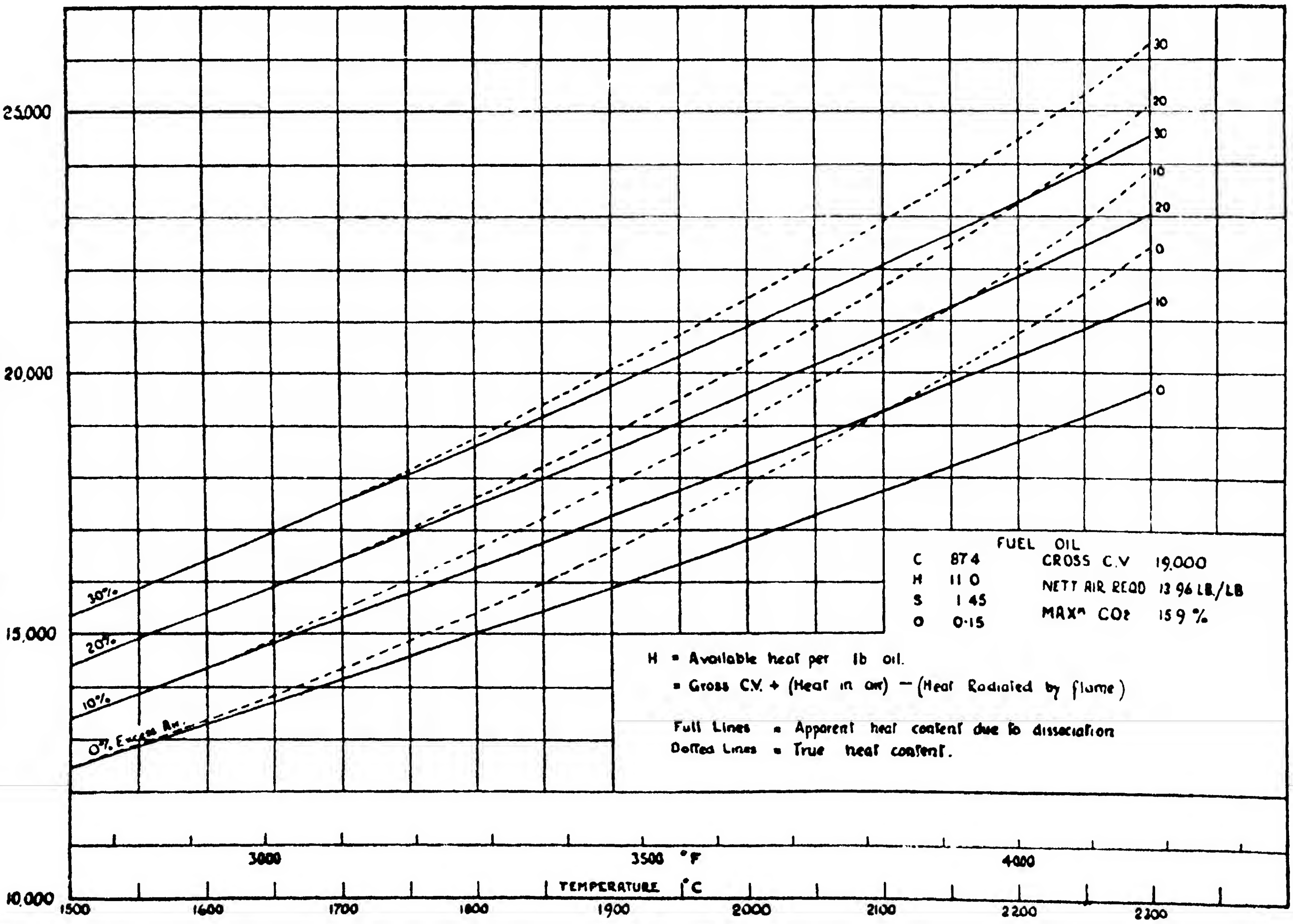


FIG. 2. Effect of dissociation on flame temperature.

(*a*) Vaporizing Burners.

The vaporizing burner has been developed with the object of eliminating the necessity of having some form of external power such as is required for an atomizing burner. There are a number of different types, two of which are described here.

These appliances operate substantially on the principle of vaporizing the oil preparatory to burning. They are therefore most successful on kerosine or refined distillates. With gas oil and heavier distillates cumulative carbon deposits tend to form, particularly at or near the points of entry of the oil. Occasionally attempts are made to use blends containing asphaltic or waxy residual oil, but results are usually poor unless continual cleaning or raking takes place. For most applications, moreover, it is found practically impossible to work with more than 7% or 8% CO_2 without the formation of smoke. Higher CO_2 and hence more effective air/oil mixing can only be achieved by special apparatus involving a vibratory type of combustion or similar artifice. Certain recent patent applications disclose attempts to obtain high air preheats in order to keep down carbon formation, while there are several commercial burners for which good results are claimed when using water with the oil to assist gasification.

Fig. 3 shows a typical burner of the vaporizing type. The burner itself consists of a cast-iron or steel pot (1) which is perforated round the periphery with a number of small holes (2), through which part of the combustion air is drawn. In some forms of this appliance a drip feed is used which results in the oil vaporizing as it enters the vessel. No oil level builds up except at startingor with the flow set too high. Combustion begins in the pot, and sufficient heat is generated there to vaporize the oil without cracking it. The remainder of the combustion air is introduced at the point (4). This is a clearance space between the top of the pot and the bottom of the furnace. An overflow is usually provided at the bottom of the pot to a small bucket which is connected to an oil shut-off valve. In the event of flame failure the oil overflows, the bucket fills, and the additional weight causes the valve to close.

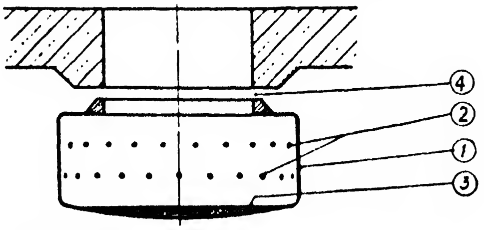


FIG. 3. Natural draught or vaporizing burner.

Fig. 4 illustrates an appliance known as the 'Range Burner'. Oil is fed from the pipe (1) to the concentric annular grooves (2) which are usually fitted with asbestos wicks (3). The vapour formed rises up the space (4) and meets air which is drawn in through the holes (5). Partial combustion takes place in the space (4) and it is completed at the point (6).

It should be noted that in both the cases cited the phenomenon known as 'reversed' combustion is taking place. It is possible to burn either a jet of combustible gas in an atmosphere of air or a jet of air in an atmosphere of the gas. In the case of the burners shown a large number of small jets of air entering at the holes are burning in an atmosphere of oil gas.

The vaporizing burner is not used to any great extent for industrial furnace work, and its most important application is in connexion with cooking ranges, particularly in localities where electric power is not available for driving fans or compressors.

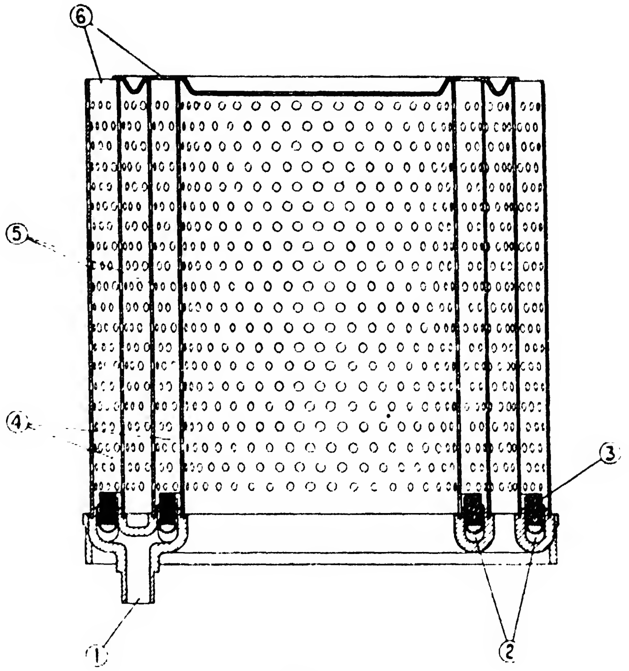


FIG. 4.

(*a*) Atomizing Burners.

The majority of oil-burning appliances work on the principle of forming a fine spray or mist, and combustion takes place with the oil in suspension. The production of this mist requires some form of power which is taken from an external source except in the case of the self-generating burners.

A number of different makes of burners is on the market, but nearly all of these can be classified under one of several main types. A few are combinations of two or more systems.

The various types of atomization are commonly known by the following names:

(i) Pressure jet.
(ii) Steam jet.
(iii) Air jet including high-pressure air, medium-pressure air, low-pressure air.
(iv) Spinning cup or rotary.
(v) Pot type.
(vi) Self-generating.

(i) **Pressure Jet.** Since this type of burner is mainly employed for steam raising, it is dealt with fully in the section headed The Use of Fuel Oil for Steam Raising. In order, however, to give here a comprehensive list of burner types it is necessary to touch on the general principles.

The pressure jet derives its name from the fact that the oil at a high pressure is forced through a special atomizer. A rotational velocity is imparted to the oil in a vortex chamber before it enters the final orifice, and as a result the oil on issuing breaks into a fine spray, approximately in the form of a hollow cone.

(ii) **Steam Jet.** A full description of the steam-jet burner is given in The Use of Fuel Oil for Steam Raising. Since the principle of this burner is almost identical with that of the high-pressure air burner, most of the factors enumerated below hold for both types.

(iii) **Air Jet.** In the case of the air-jet burner atomization is carried out by means of a stream of air. The pressure employed may range from ¼ lb. per sq. in. up to 100 lb. per sq. in. or more, and for this reason burners of this type are usually divided into three classes—'high-pressure air', 'medium-pressure air', and 'low-pressure air'. Although the fundamental principles are the same for all the burners under this heading, the design is affected by the air pressure in use and the proportion of air taken through the burner. It is impossible to make an exact demarcation between the different groups, but as a rough classification the following pressure ranges may be taken:

High-pressure air.	5 lb. per sq. in. and upwards.
Medium-pressure air	1½ lb. up to 5 lb. per sq. in.
Low-pressure air.	¼ lb. up to 1½ lb. per sq. in.

Fig. 5 illustrates a typical burner nozzle operating on high-pressure air. The oil flows through a central tube, and on emerging is caught up by a stream of air moving at high velocity. This has the effect of breaking up the oil stream into a fine mist.

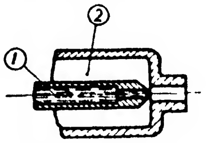


FIG. 5. High-pressure air or steam-jet nozzle (with atomizing agent outside).

The opening through which the air issues is adjustable by screwing the final nozzle backwards or forwards. This has the effect of controlling the quantity of air while maintaining the maximum velocity, and it is therefore a better method than by throttling on an outside valve.

It is well known from elementary theory that when operating with air at pressures above 13 lb. per sq. in. some form of convergent-divergent nozzle should be used in order to obtain the highest velocity of the air stream. An examination of a large number of high-pressure air burners reveals the fact that no serious attempt on these lines has been made, and this is probably due to the fact that in practice the maximum theoretical velocity is obtainable from a compressed air jet with a negligible amount of divergence. In the case of steam issuing from a jet at high pressure the angle of divergence requires to be considerably greater than with air, and in some steam-jet burners this fact is taken into account.

Fig. 6 illustrates a high-pressure air or steam-jet burner in which the atomizing agent enters through the centre of the oil spray. This burner is shown for use with steam, and a slight divergence exists, therefore, on the inner nozzle.

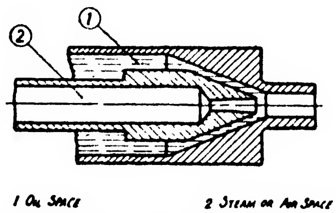


FIG. 6. High-pressure air or steam-jet nozzle (with atomizing agent inside).

Fig. 7 shows one of the most elementary types, which is usually known as the scent-spray burner. The oil is maintained at a constant level slightly below the tip of the vertical oil nozzle. Steam or compressed air is blown past this nozzle, sucks the oil up, and atomizes it.

In connexion with air-jet burners as a whole the quantity of air used for atomization resolves itself into a question of the momentum of the air and oil streams. It is therefore obvious that with the high velocities which are obtainable from high pressures a given velocity can be imparted to the oil with a smaller quantity of high-pressure air than is the case if a lower air pressure is employed. The exact proportion of the total air used for atomization depends on the construction of the burner, but from consideration of power requirements to compress this air it is obviously desirable to keep the quantity at a minimum.

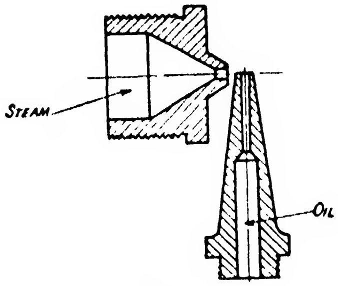


FIG. 7.

Figs. 8, 9, and 10 show three different forms of medium-pressure air burners, although it must be understood that with correct clearances these burner types are equally suitable for steam or high-pressure air.

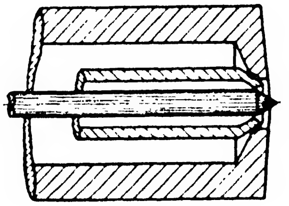


FIG. 8.

In Fig. 8 the oil runs parallel with the air, whereas in the burner shown in Fig. 9 the oil enters at right angles to the air.

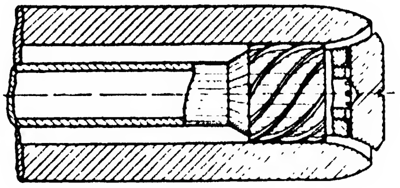


FIG. 9.

In the burner shown in Fig. 10 a special swirl chamber (4) is provided. Air enters through the tangential air holes and the mixture of oil and air is caused to rotate rapidly before leaving the burner nozzle.

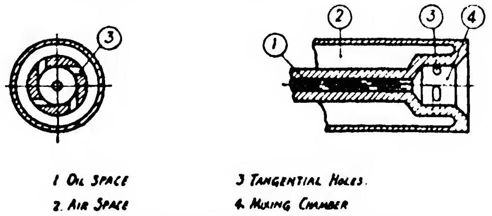


FIG. 10. Medium-pressure air burner.

Some of these burners operate over a wide range of pressures, such as from ¼ lb. per sq. in. up to 5 lb. per sq. in. They virtually become, therefore, low-pressure air burners at the lower end of the scale and, as mentioned above, high-pressure burners at the other end. On account of this, the medium-pressure burner has a wide oil consumption range and it is frequently used for applications which require considerable variations in fuel consumption. This particularly applies to the firing of intermittently operated ceramic kilns.

The low-pressure air type of burner has its greatest sufficient to raise this oil to the top of the jet, at which point it is caught up by the steam jet and a fine spray is formed.

In order to produce the steam, water is fed to the flash boiler. A steady flow of water is supplied from the water tank by means of air pressure. The air pressure is generated by a hand pump, and two or three strokes per hour are sufficient to maintain the pressure during steady operation. It should be noted that the steam-generating tubes are arranged on each side of the centre line of the burner.

With some types of self-generating burners it is necessary to light a fire of oily waste and to raise a quantity of steam in the coil or boiler before the burner can be started. With the special type illustrated, initial atomization is performed by compressed air from the hand pump, and a flame is maintained in this manner until sufficient steam has been generated in the coil to permit changing over. A three-way cock is provided for this purpose. In one position it connects the air space at the top of the water tank with the coils, and thus affords a path to the atomizing jet. In the second position connexion is made to the water at the bottom of the reservoir, and in the third position all connexions are cut off. For further details of burner types, including general history of burner development, see Ir. H. A. Romp, Oil Burning [7].

3. Power Consumption

Table I below gives a comparison between the various types of burners as regards the power required for atomization and the minimum weight of atomizing agent which is required.

The velocities of the mixture at various points are calculated from the theory of conservation of momentum, i.e.

$$M_1V_1+M_2V_2 = (M_1+M_2)V_4$$
$$(M_1+M_2)V_4+M_3V_3 = (M_1+M_2+M_3)V_5,$$

where M_1 = mass of atomizing agent (air or steam) in lb.,
M_2 = mass of oil in lb.,
M_3 = mass of secondary air in lb.,
V_1 = velocity of atomizing air or steam calculated from pressure drop,
V_2 = initial velocity of oil (assumed zero except for pressure jet),
V_3 = velocity of secondary air,
V_4 = velocity of atomized mixture,
V_5 = velocity of final combustion mixture.

The values of V_1 for air discharging through nozzles at various pressures are shown on Fig. 16.

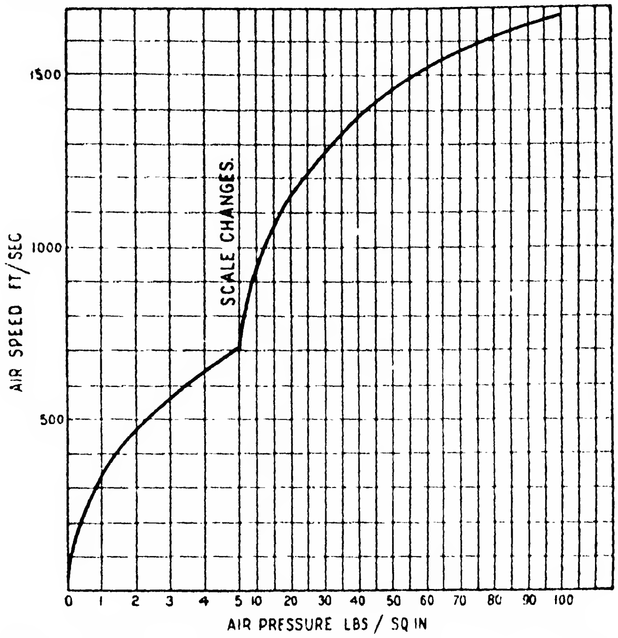


FIG. 16. Chart showing relationship of air pressure and maximum theoretical speed.

TABLE I

Method of atomization	Gauge pressure lb. per sq. in.	Velocities, feet per second V_1 Atomizing air or steam	V_2 Oil	V_4† Atomized mixture	V_5† Combustion mixture	M_1 = wt. of atomizing agent lb. per lb. oil (minimum)	Percentage of total combustion air ‡	H.P. for atomizing 100 lb. oil per hr.§
Steam	30	2,140	..	494	33·3	0·3	..	
Air: High pressure	100	1,650	..	436	31·3	0·36	2·0	1·76
	20	1,160	..	332	24·4	0·4	2·2	1·20
	10	930	..	289	22	0·45	2·5	0·62
Medium pressure	5	712	..	250	20·3	0·54	3·0	0·4
	3	577	..	248	22·8	0·75	4·2	0·39
Low pressure	1	341	..	236	40·4	2·25	12·5	0·375
	0·5	244	..	191	46·5	3·6	20	0·35
	0·25	175	..	151	58	6·3	35	0·31
Pressure jet	100	.	126	126	6·7	..	..	0·021
*Pressure (V_3 = 20)	100	..	126	126	25·7	..	..	0·021
Air at low pressure	1	341	..	323	323	18	100	3·0
	0·5	244	..	231	231	18	100	1·76
	0·25	175	..	166	166	18	100	0·88

* Combustion secondary air is assumed to enter furnace under natural draught at negligible velocity. This is not true in most cases, and the effect of a small velocity V_3 is illustrated under the last case for pressure jet where V_3 has been taken at 20 ft. per sec.

† V_4 and V_5 give the resultant atomized and combustion speeds as calculated from the momentum equations. These speeds are not necessarily in a forward direction, since a rotational movement is usually introduced.

‡ The percentage of combustion air is based on the assumption that combustion is taking place with 30% excess air, i.e. approximately 18 lb. of air per lb. of oil.

§ This is the net H.P. required for supplying the atomizing agent at the stated pressure. It does not allow for frictional pressure drop in pipelines, nor is any allowance made for supplying secondary combustion air by forced or induced draught.

In the case where it is decided to take all the combustion air through a low-pressure air burner the horse-power absorbed would be increased as shown in the lower section of Table I.

The mixture speeds and percentage air for atomization shown in Table I are plotted in Fig. 17. Referring to Table I two examples have been shown for the pressure jet. In the first case it is assumed that initially the combustion air is stationary. This condition would never arise in practice since the combustion air enters the furnace round the burner at a considerable speed. The latter is illustrated in the second pressure jet case of the table where the combustion air is assumed to have an initial speed of 20 ft. per sec. The resultant speed of the mixture becomes 25·7 per sec. This probably represents the minimum mixture speed likely to be encountered in practice, since with all the other types of burners the secondary air will usually have an appreciable initial speed.

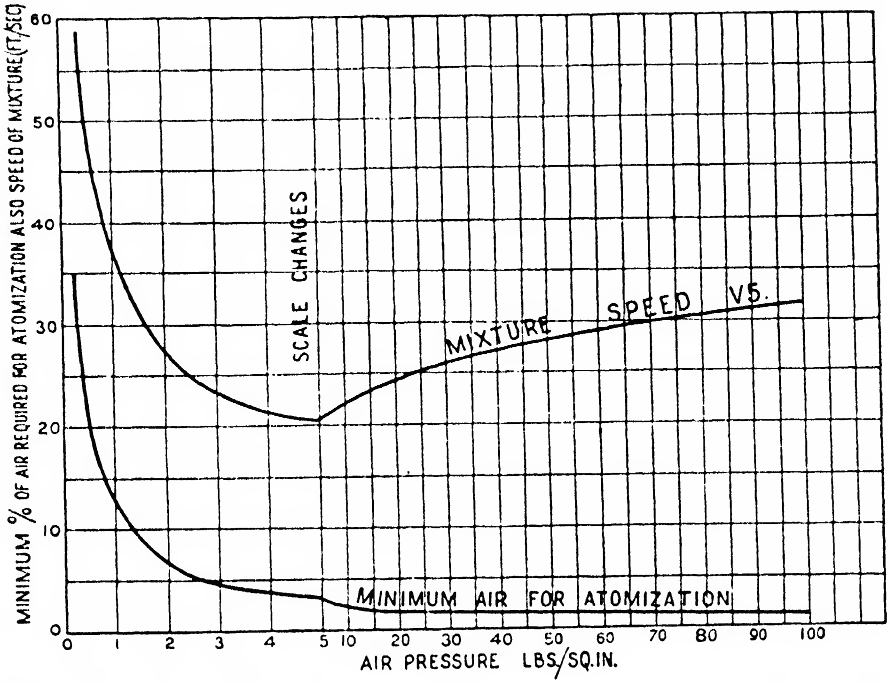


Fig. 17. Chart showing minimum atomizing air and mixture speeds plotted against air pressure.

This resultant mixture speed is not entirely in a forward direction since considerable swirl is often imparted to the primary and secondary combustion air with a view to creating turbulence. From the standpoint of an approximate criterion of atomizing effect, however, the method given appears to fit in with practical results.

It will be noted from Table I that the last column gives the power consumption with various systems. The pressure-jet system would appear to involve the least power. It should be noted, however, that where assisted draught is used, allowance must be made for the power required to drive the fans. The pressure-jet system is not used as freely as other types for industrial furnaces, owing to the fact that the flame is usually too wide and lacks the torch-like directional effect obtainable with other atomizing methods.

The low-pressure air system is employed for the majority of oil-fired industrial heating operations, and it has an advantage in that the combustion air can be heated to a temperature of 500° F. to 600° F. before it is passed through the burner. Where it is essential to employ a higher air preheat, such air would usually be admitted to the furnace through ports near the burner. In this case, one would choose the high-pressure or medium-pressure air system, taking the minimum quantity of cold air through the burner.

4. Secondary Air

It is necessary in practically all cases to arrange for secondary air to be supplied. The only exception to this rule is the low-pressure air burner arranged to take 100% of the combustion air through the burner. Fig. 18 indicates a mounting for this last case. The opening in the furnace wall is arranged to be of the same diameter as the outside of the burner nozzle. By this means very little air enters the furnace other than through the burner. In those cases where it is necessary to induce only a small proportion of the combustion air an arrangement similar to Fig. 19 can be used. The quantity of air induced is controlled by metal slides round the opening or by altering the furnace damper setting.

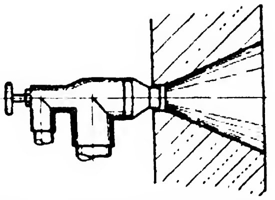


Fig. 18. Low-pressure air burner passing all combustion air.

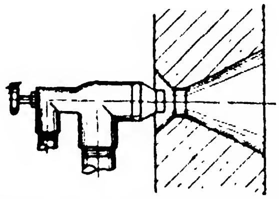


Fig. 19. Low-pressure air burner injecting part of combustion air.

Fig. 20 illustrates what is known as the 'hit and miss' air director. This consists of a number of slots in a steel plate arranged radially round the burner. Control is effected by rotation of a similar plate which is in contact with the other. This arrangement gives poor mixing and is not to be recommended.

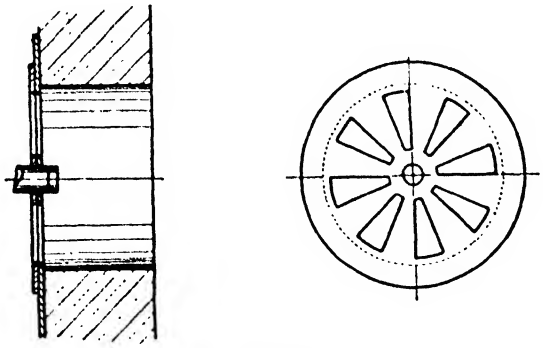


Fig. 20.

The best arrangement of air director is the cylindrical type with provision for mixing in a venturi throat as shown in Fig. 21. A swirl can be imparted to the air if required. This type can be used with natural or induced draught, and, if desired, a casing can be arranged round the outside and a supply of air delivered to this under forced draught.

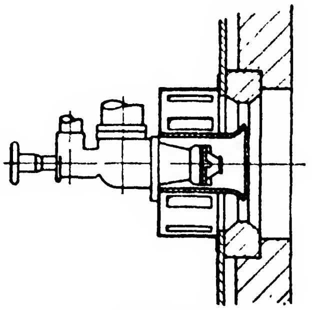


Fig. 21.

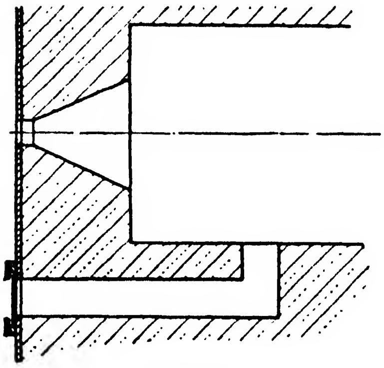


Fig. 22.

Fig. 22 depicts an air port leading into the combustion chamber at some distance from the burner. This is sometimes used where comparatively delayed combustion is required.

The method shown in Fig. 23 is usually satisfactory for medium pressure air burners. The air enters the furnace through a long, narrow slot under the burner centre line.

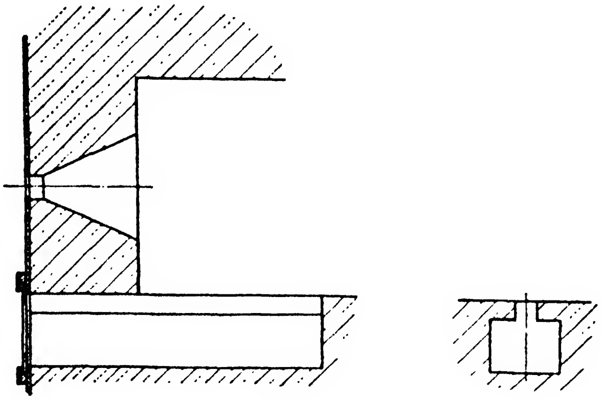


Fig. 23.

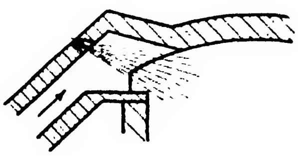


Fig. 24.

A modification of this, in which the combustion chamber floor is perforated, is also used to some extent.

With preheated air at moderate temperatures the air can be supplied to a steel air director under forced draught, as mentioned under the description of Fig. 21. With higher temperatures steel cannot be used, and the air may enter under the burner as in Fig. 24 or through holes in a special fire-brick quarl as in Fig. 25.

Fig. 25.

5. Combustion Chambers and Refractories

An oil burner should be capable of maintaining satisfactory combustion without the assistance of any incandescent brickwork. However, a suitably proportioned combustion chamber lined with refractory material can perform several valuable functions in respect to:

(*a*) Accelerating combustion;
(*b*) Promoting good mixing;
and (*c*) In the case of direct fired furnaces increasing the rate of heat transfer by radiation.

The combustion chamber volume required for a given fuel consumption rate depends on a number of factors. In practice wide variations occur and rates are employed from 2½ lb. of oil per hour per cu. ft. of combustion space up to ten times as much. This corresponds to a heat liberation rate of 47,500 B.Th.U. per hour per cu. ft. up to 475,000 B.Th.U. per hour per cu. ft.

No hard and fast rule can be laid down for the rate to be employed in any particular instance since each application must be treated on its own merits. It may be stated, however, that the rate of 2½ lb. per cu. ft. applies to the combustion chambers of boilers operating on average low chimney draught, and the highest rate quoted may be used in extreme cases for very high temperature work such as in welding furnaces. This rate is also encountered on certain applications where space is of vital importance, such as boilers for naval work and for use on steam railcars.

The combustion chamber walls, roof, and floor of an oil-fired furnace are subjected to high temperatures, thus necessitating a refractory material of suitable quality. While the first essential factor is that the refractory should have a high melting-point, this is not the only consideration. In fact, it is more important to have a high temperature softening-point under load than a high melting-point. This arises from the fact that there is, as a rule, no sharply defined melting-point, most refractories beginning to soften at much lower temperatures.

When a furnace is used intermittently it is essential that the refractory should have a smooth expansion curve. Most of the expansion of silica takes place below 1,500° F. It is therefore necessary to take great care that a furnace is brought up to temperature very slowly when this material is used. Rapid heating results in a form of surface flaking known as 'spalling', and on this account silica should only be used in furnaces which are worked continuously and which are very rarely allowed to cool. For applications of this nature, such as the crowns of glass tanks, silica gives excellent service, but when a furnace has to be brought up to temperature rapidly it is usual to employ a fire-brick containing a high percentage of alumina. The best quality of high aluminous fire-brick contains approximately 45% Al_2O_3, the remainder being mainly SiO_2 with very small proportions of impurities such as ferric oxide. The analysis corresponds approximately to Al_2O_3, $2SiO_2$.

For applications where very high temperatures are experienced other more expensive refractories are sometimes used. These include sillimanite (Al_2O_3, SiO_2); mullite ($3Al_2O_3$, $2SiO_2$); corundum (Al_2O_3), and silicon carbide (SiC). To minimize heat losses from the combustion chamber, insulation can be resorted to with advantage. Few of the commercial insulating materials can be subjected to temperatures above 1,800° F. A layer of refractory, therefore, must be interposed between the flame and the insulating material. The thickness of this layer must take into account both the stability of the furnace structure and the maximum temperature which is permissible on the insulation.

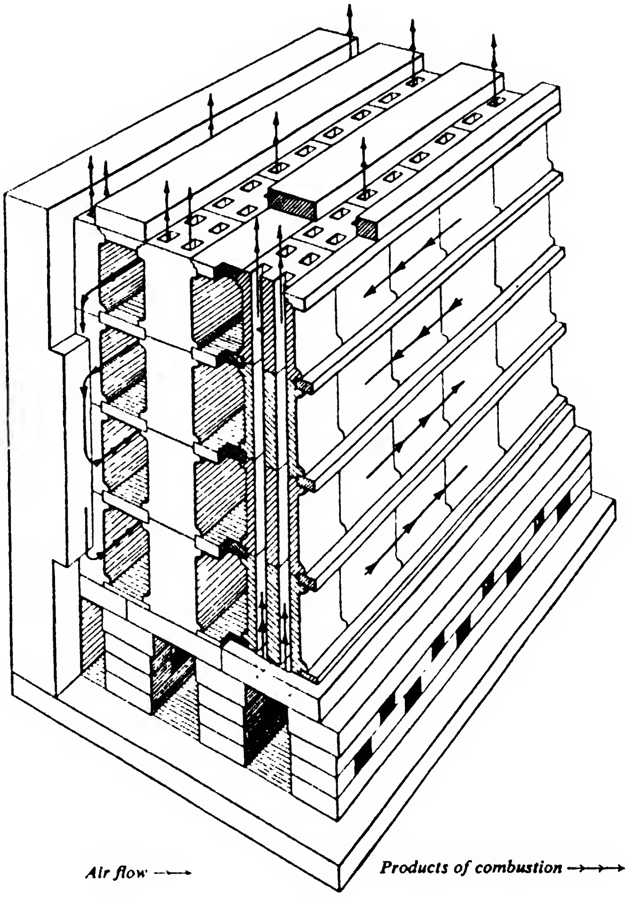


FIG. 26.

6. Air Preheating

The effect of preheating the combustion air is threefold:

(*a*) The flame temperature is raised, resulting in increased heat transfer.

(*b*) The rate of combustion is increased, thereby further facilitating the production of high temperature.

(*c*) A considerable reduction in fuel consumption is brought about.

There are two systems in use for abstracting the waste heat from the flue gases and delivering it to the combustion air. These are respectively recuperators and regenerators. In a recuperator the air and flue gas flow in separate ducts and heat is transmitted from the flue gas to the air through the dividing wall. With the regenerative system the air and flue gas flow alternately over the same surface. During one portion of the cycle the flue gas gives up heat to the surface, and for the remainder of the cycle this heat is 'wiped off' by the air.

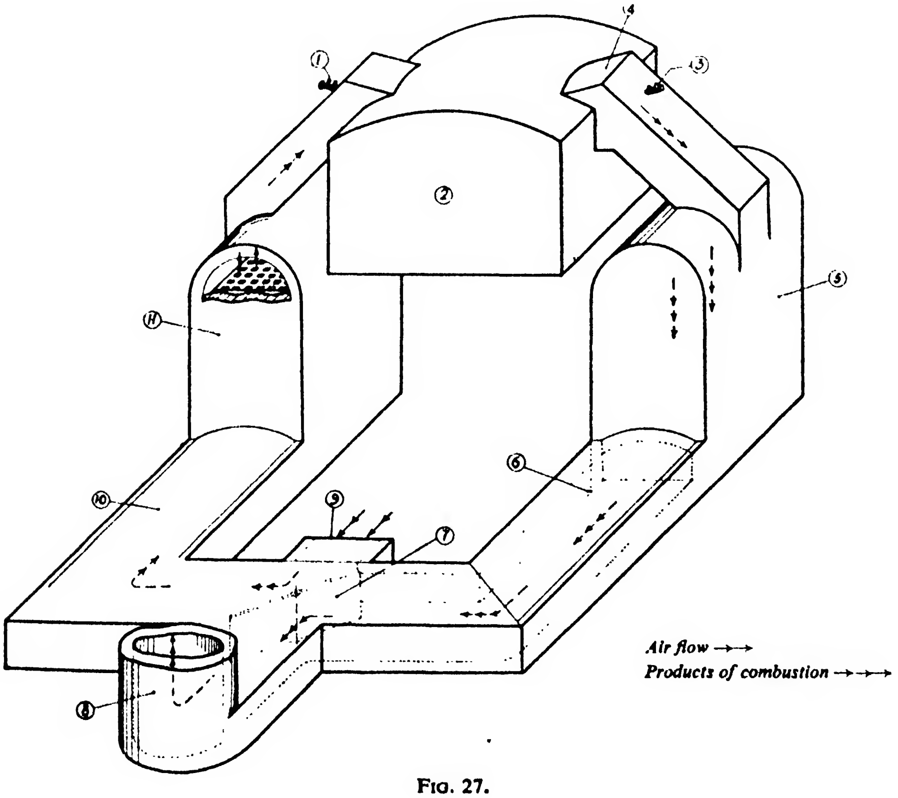


FIG. 27.

(i) **Recuperation.** For air temperatures up to about 800° F. a steel tubular air heater is suitable, provided precautions are taken to limit the pipe temperature to a safe figure. If higher temperatures are employed, the rate of scaling for mild steel increases rapidly.

For higher temperatures a refractory recuperator should be used. There are a number of proprietary makes, all of which differ in regard to the design of the refractory elements from which the recuperator is constructed. Fig. 26 illustrates the Chapman Stein recuperator.

(ii) **Regeneration.** For high temperature furnaces in continuous operation the regenerative system is usually employed.

Fig. 27 shows an orthographic projection of an oil-fired furnace with regenerators. The arrows indicate the air and gas flow when the burner (1) is alight. At definite intervals burner (1) is extinguished, burner (3) is put into action, and the direction of flow is reversed by turning the reversing valve (7) through an angle of 90°. The regenerators are indicated by (5) and (11).

For the direction of flow shown, the burner (1) fires into the furnace (2) and the gases leave by the port (4), entering the regenerator chamber (5) which is packed with checker brickwork. The hot gases flow through passages in this brickwork and give up their heat. They then leave the regenerator by the flue (6) and pass the reversing valve (7) on their way to the chimney (8).

The air required for combustion enters at (9) and flows by the flue (10) to the other regenerator (11) where heat is picked up from the brickwork. This heat had been given to the brickwork by the flue gases during the previous reversal.

7. Viscous Fuels

The types of burners described can handle all the fuel oils of commerce when suitable precautions are taken to provide any oil preheat which may be necessary. The heaviest grade sold is usually 'Bunker C', having a viscosity of about 6,000 sec. Redwood No. 1 at 100° F. Such a grade is burnt in large quantities under boilers in ships, utilizing pressure-jet burners with standard pumping and heating sets.

Beyond Bunker C grade there is a varied number of heavy and viscous residues, refinery wastes, and asphalts. These do not usually find their way on to the open market, but are burnt at the oil refineries. The problems associated with the burning of such residues are more in connexion with the preparation of the fuel than with the actual atomizing apparatus. With such fuels as asphalt which are solid at ordinary temperatures, provision must be made for continuous circulation of hot oil. In addition there must be adequate facilities for draining any section of the pipeline or burner apparatus, as these must be cleared whenever a shut-down occurs. Temperatures as high as 200° C. would be required for asphalt, but when this temperature is obtained a normal pressure-jet burner functions adequately.

Moderately heavy refinery residues such as Dubbs's are frequently burnt quite successfully with low air pressure or rotary burners. These residues must be heated to such a temperature as to reduce the viscosity down to approximately 100 to 200 sec. Redwood No. 1. Although the burners mentioned are successful under favourable conditions, on the whole at most refineries steam atomization is preferred, and a burner of the internal mixing type is usually chosen. In some cases the residue is propelled mechanically within the burner to assist uniform flow.

Acid sludge and similar very difficult residues can be burnt by utilizing the steam-jet method of atomization, and again the internal mixing type is preferred. It is difficult to obtain really satisfactory combustion with such fuels, but the problem of disposal is usually so difficult that it is desirable to burn such fuels so as to save the high cost of dumping.

8. Handling and Storage

For storing fuel oil, tanks made from mild steel plate are almost invariably used. The steel should not be galvanized.

Concrete tanks are occasionally used, but it is essential that the concrete should be coated with a suitable oil-resisting compound since by itself it is porous to oil. In any case the greatest care must be exercised to provide against cracks due to setting and ageing.

Occasionally small storage tanks are buried underground, and although this method saves space, there are several strong objections to it:

(*a*) It is almost impossible to detect a leak until it has grown to serious dimensions.

(*b*) Sludge and sediment cannot be drained from the tank without a considerable amount of trouble.

(*c*) Corrosion of the tank may take place.

Some of the more important precautions to be taken in storing fuel oil are given below:

(i) It is usually desirable when placing a storage tank within a building to surround it with a reasonably oil-tight catchpit capable of holding a minimum of, say, 80% of the contents of the tank, as a safeguard against a serious leak or the fracture of a valve.

(ii) Each tank should have a vent of such a size as to allow rapid filling without undue pressure building up in the tank. The vent pipe should be led into the open air.

(iii) Tanks in exposed positions where sharp frosts are likely to occur should have main valves of cast steel, preferably lagged, while bends, tees, and similar fittings are better of wrought iron or cast steel. Cases have arisen where pockets of water settling out in cast-iron valves or fittings have caused fracture in severe frosts.

(iv) On comparatively large storage tanks (say, 100 tons capacity and over) a valuable safeguard against the fracture of the main stop-valve of the tank is to have an internal foot-valve which can be operated by links from the outside.

(v) For large storage tanks on very poor or waterlogged foundations, there should be a flexible connexion in the main pipeline leading from the tank.

(vi) Gauge glasses should not be used on storage tanks.

(vii) The draw-off pipe from a tank is usually taken some distance from the bottom so as to leave a sludge space.

(viii) A sludge or drain valve should always be fitted at the lowest part of a tank so as to facilitate removal of water or sludge at frequent intervals.

Many burner systems are supplied with oil by gravity, and in these cases some form of service tank is required. This is arranged at a suitable height above the burner level. The capacity should be such that one day's supply is stored, and the tank can therefore be filled at convenient intervals by a pump drawing from the main storage tank which is usually at a lower level. This pump is either hand-operated or motor-driven. In the latter case a float-operated switch can be incorporated which starts the pump when the level drops to a certain point and switches it off when the tank is full. Fig. 28 shows diagrammatically a simple gravity system for supplying a light fuel oil.

When a number of furnaces have to be served from a common supply, it is frequently advisable to utilize a ring main in which oil is constantly circulated by a pump. This is particularly advisable when a heavy oil is in use which requires to be heated. By adopting the circulating system with correctly proportioned and insulated lines it is possible to obtain an oil supply to all the furnaces at a fairly uniform pressure and temperature.

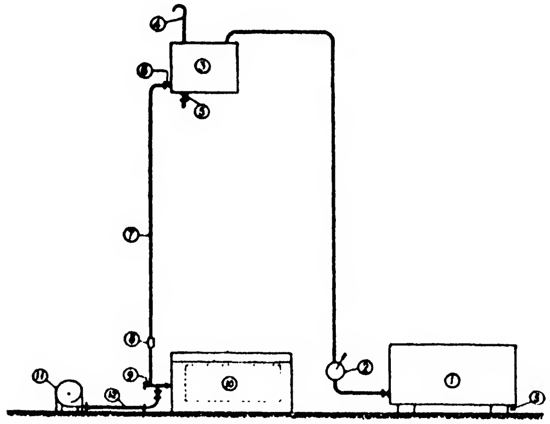
Fuel oil is heated with the following objects in view:

(*a*) to reduce the viscosity for pumping purposes;

(*b*) to improve the burning characteristics in a furnace;

(*c*) for cleaning purposes to facilitate the removal of water and dirt by settling or centrifuging.

Very light fuel oils of the nature of gas oil require no heating either for handling purposes or to improve the burning properties.

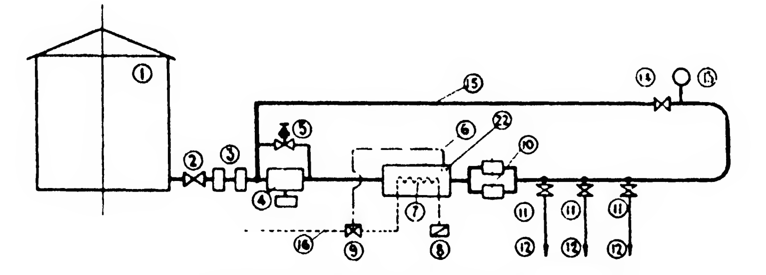


1 Main Storage Tank
2 Oil Pump for Filling Service Tank
3 Daily Service Tank
4 Vent Pipe
5 Drain Valve for Sediment
6 Outlet Valve
7 Delivery Line to Burner
8. Filter
9. Oil Burner
10. Furnace
11. Blower for supplying Atomising Air
12. Air Pipe to Burner.

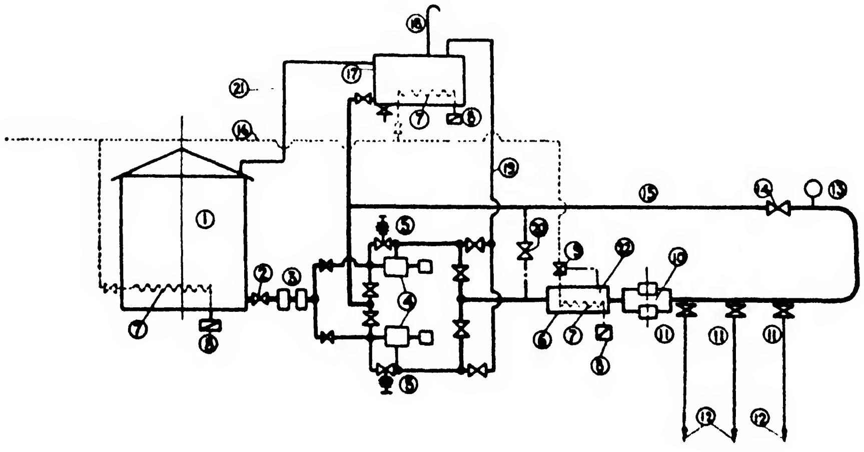
FIG. 28. Simple gravity supply system for a light fuel oil requiring no preheating.

Fig. 29 shows two typical heavy fuel-oil installations in diagrammatic form. At *A* is indicated a system for use with moderately heavy fuel oil which is pumpable at ordinary temperatures. The oil flows from the main storage tank (1) through a filter (3) to the pump (4). It is then circulated through a line heater (6) and a further filter (10) to the burner control valves (11). A constant pressure can be maintained on the line by means of the valve (14) and a pressure gauge (13). This valve may be either manually operated or it may be a spring-loaded valve which can be set to discharge at a definite pressure difference. The surplus oil which is not used by the burners returns along the line (15) to the pump suction.

Where a heavier fuel oil is in use which does not flow readily it may be necessary to install heating coils in the main storage tank, and furthermore it may be advisable to provide settling tanks. A diagram on these lines is shown in Fig. 29 B. In this case two pumps are indicated, one of which acts as a stand-by in case the other breaks down. Also with the arrangement shown one of the pumps can be used for circulating oil to the burners while the other is drawing oil from the main storage tank and pumping it into the settling tank. Nearly all fuel oil contains a small percentage of water, and frequently this does not settle out until the oil is heated. It is therefore advisable with very heavy oils to provide tanks where the oil can be maintained at a constant temperature for some time before it is used, and a drain valve should be fitted at the bottom of the tank for drawing off water and sediment. This latter remark applies to all oil tanks whether they are to be used for light or heavy oil. For further details refer to Lubbock, 'The Storage, Handling and Transmission of Liquid Fuel by the User' [4].



A MODERATELY HEAVY FUEL PUMPABLE AT ORDINARY TEMPERATURES ~ NO PREHEATING IN MAIN TANK



B THICK FUEL OIL WITH PREHEATING IN MAIN TANK AND AUXILIARY SETTLING TANK ~ DUPLEX PUMPS

KEY

ITEM Nº	DESCRIPTION
1	MAIN STORAGE TANK
2	OIL VALVE
3	OIL FILTER
4	OIL PUMP
5	RELIEF VALVE
6	HEATER VESSEL
7	STEAM COIL
8	STEAM TRAP
9	THERMOSTATIC STEAM VALVE
10	DUPLEX OIL FILTER
11	BURNER CONTROL VALVES
12	OIL BURNERS
13	PRESSURE GAUGE
14	PRESSURE CONTROL VALVE
15	OIL RETURN MAIN
16	STEAM MAIN
17	SETTLING TANK
18	VENT
19	FILLING PIPE FOR SETTLING TANK
20	BYE-PASS FOR GRAVITY OPERATION
21	OVERFLOW - RETURN TO MAIN STORAGE
22	THERMOSTAT

FIG. 29.

II. APPLICATIONS

1. Domestic Uses

(i) **Central Heating.** Oil fuel is used extensively for central heating in offices, factories, churches, hospitals, cinemas, and many other types of buildings, apart from the large field represented by private dwelling-houses. In some large public buildings the heating installation may be of the industrial type with the corresponding oil-burning plant. There is, however, at present an increasing tendency towards the use of the unit type of burner, completely automatic in action and operating under thermostatic control. This is the case with most dwelling-houses where oil is used, and the magnitude of this development will be realized from the fact that in the U.S.A. about one million automatic oil burners are installed for domestic use. These consume per annum approximately six million tons of central-heating oil, most of which would be classed as a gas-oil distillate.

From the technical point of view, in these burners no new principles of atomization are introduced, the novelty of the development lying in the combination of burner, motor, fan, pump, and such-like into a compact unit including automatic control apparatus. The type of atomization which has been adopted by most designers is the pressure jet, owing to its simplicity of design, cheapness, comparative silence, and the constant metering provided by the final pressure-jet orifice. Although it is for the time being the most popular type, side by side with the pressure jet, the medium-pressure burner and the rotary have made steady progress.

The chief feature of most of these burners lies in the provision of a thermostat or pressure sensitive device for automatically starting the motor and lighting the burner when heat is required. The burner is arranged to shut down when a given temperature or pressure is reached. Ignition is usually by electric spark from a high-tension transformer operating at about 10,000 volts. Other ignition means are successfully used, such as the fixed or expanding gas jet, the electric spark cum gas jet, and the resistor type of ignition rod.

Linked with these units is an electric control system providing safety devices against all contingencies including failure to ignite, loss of flame, failure of electric supply, loss of oil, and such-like.

A very large number of electrical systems has been evolved for this purpose, which it would be beyond the compass of this article to describe in detail. The general principle on which most circuits operate can be followed from Fig. 30, where an instrument, which can be described generically as the 'combustion safety device', acts as the master controlling appliance. In most instances the combustion safety device is a 'stack-switch', 'flue thermostat', or equivalent instrument, which is affected by the formation of flame when the burner lights and thus initiates a cycle of operation in the remainder of the controlling circuit. This ensures that the burner cannot continue to run if ignition is not satisfactorily established or if the flame once formed should fail at any subsequent time.

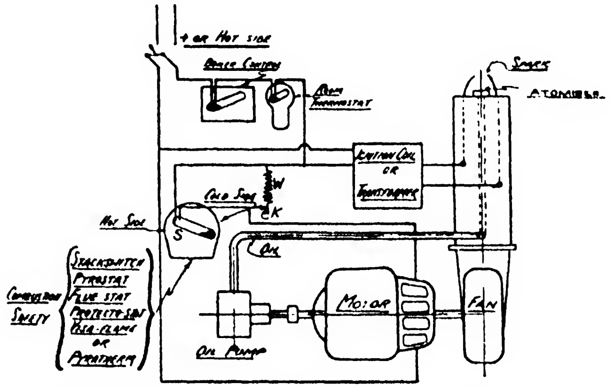


FIG. 30. Elementary wiring diagram with safety device

In all these circuits there is a timing device which controls the period during which the motor of the burner is allowed to operate before a safety lock-out occurs. One simple way of doing this is shown in Fig. 30 where the circuit to the burner motor passes initially through a resistance wire wound on a bi-metallic blade. If flame forms and the combustion safety device responds correctly by moving over from the 'cold' to the 'hot' side, this path through the

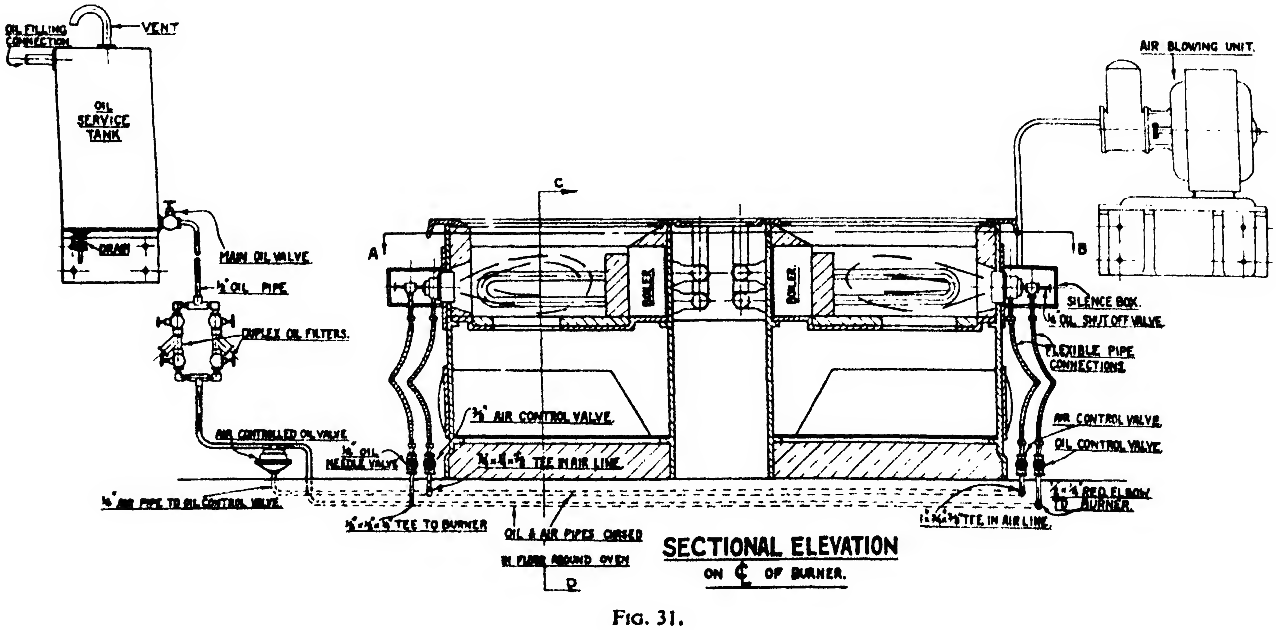


FIG. 31.

resistance element is short-circuited and a correct low resistance line is provided for the running current. If, however, the combustion safety device does not function, due to some fault, the current will continue to flow through its temporary path via the resistance on the bi-metallic blade, and the latter, warping ultimately with the heat produced, will throw the control system into its safety position where it will be locked by some mechanical trigger device.

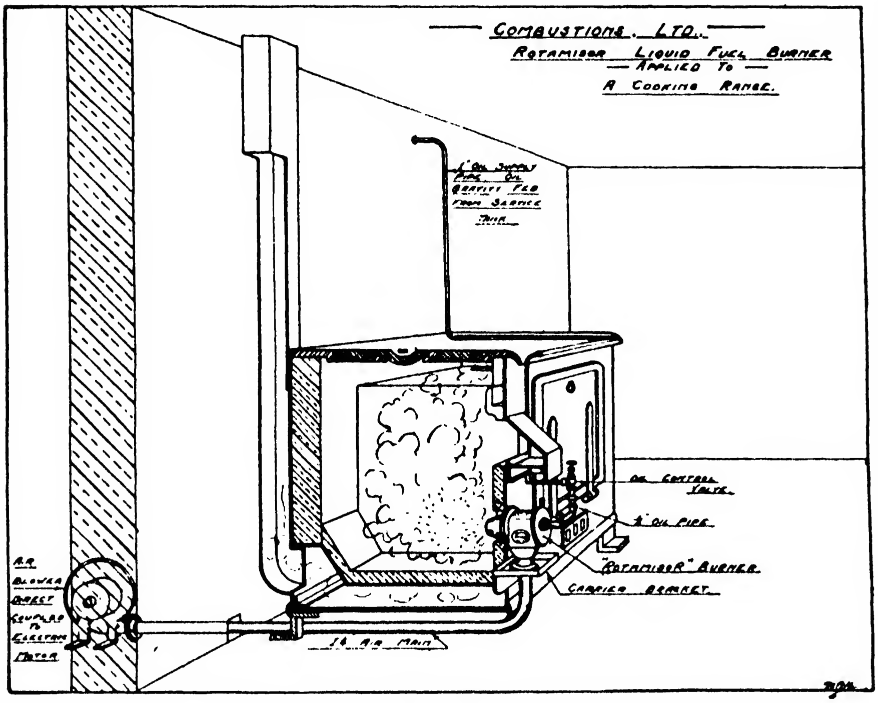


FIG. 32.

Many timing devices have been proposed and used as an alternative to the warping blade described above. One very successful control system utilizes the expansion of a bellows filled with a special liquid, the bellows itself being surrounded by a resistance winding. Other makers use clockwork mechanisms, small synchronous motors, and dash-pot devices to achieve timing conditions equivalent to the warping blade. For more detailed accounts refer to Gollin, 'Fuel Oil for Central Heating' [2]; Lubbock, 'Industrial Uses of Fuel oil' [5]; Tapp, *Handbook of Domestic Heating* [9].

(ii) **Domestic Hot Water.** Burners of the same type as described in the previous section are used for domestic hot-water boilers. In the case of residences, considerable headway has been made with a system where one hot-water boiler, with its fully automatic oil burner, is used for providing both central heating and domestic hot water. The most effective arrangement is that where a motorized valve is fitted on the heating flow main and placed under the control of the room thermostat or similar device for keeping a constant temperature in the rooms. The burner itself is then under the control of the water thermostat in the boiler. In winter, therefore, a demand for heat on the radiator side would be met by the motorized valve on the flow main opening at the response of the room thermostat. If this, together with the demand for hot water (obtained from a calorifier) resulted in a drop of boiler water temperature, the burner would be started up, assuming it had been shut down previously by a corresponding rise in temperature.

(iii) **Cooking.** Atomizing oil burners have been successfully applied for many years past to the larger types of cooking ranges. The outstanding development in this respect is for galleys of oil-fuelled ships where the same fuel is utilized for the cooking ranges as for the boilers. On such ranges practically every type of burner is represented, the most common being the medium air pressure.

In addition to ships, hotels and large private residences frequently have their ranges fitted with oil-burning equipment, typical examples of which are shown in Figs. 31 and 32.

Results in respect to oil consumption vary, of course, considerably according to the duty involved, but a typical example would be that of a large hotel where 40 gallons of oil per day were used for cooking against a reported previous coal consumption of ½ ton per day.

In addition to the comparatively large ranges utilizing atomizing oil burners, small portable cooking ranges with modern wickless vaporizing burners are coming into use on an increasing scale in different parts of the world. The burners usually chosen are those described in the early part of the article and illustrated in Figs. 3 and 4.

2. Metallurgical Applications

(i) Metal Smelting.

(*a*) **Tin.** Oil fuel is used for most of the tin smelting carried out in the world. The more important works utilize regenerative furnaces with a capacity of approximately 25 tons of ore. The burners used are of the pressure jet type, reversals of firing taking place as on a Siemens-Martin furnace. The amount of oil used per ton of metallic tin is on an average 224 lb. The outstanding advantage of oil fuel for tin smelting lies in the low metallic losses in the waste gases.

Smaller furnaces are also employed and they are usually fitted with a simple recuperator. Such furnaces would be similar to Fig. 33, although this, as described below, was actually used for smelting copper.

On a typical furnace of this type the air was preheated to 250° F. A charge of 3 tons of ore resulting in 1·7 tons of metallic tin was smelted in about 6 hours. The oil consumption was 14 gallons per hour.

(*b*) **Copper.** Copper smelting is carried out with oil fuel, and Fig. 33 indicates a small oil-fired furnace used for this purpose. The furnace is fitted with three low-pressure air burners and forced draught air directors. Cold air is passed through the burners for atomizing the oil, secondary preheated air being delivered through the forced draught casing.

Fuel consumption varies with the size of the furnace and the air preheat. With small furnaces and cold air an oil consumption of approximately 12% of the weight of charge has been recorded. This figure drops to about 8% with large furnaces and preheated air.

(ii) Sintering.

Oil-fired sintering plants are in common use. The flame is formed above the surface of the finely divided ore, and

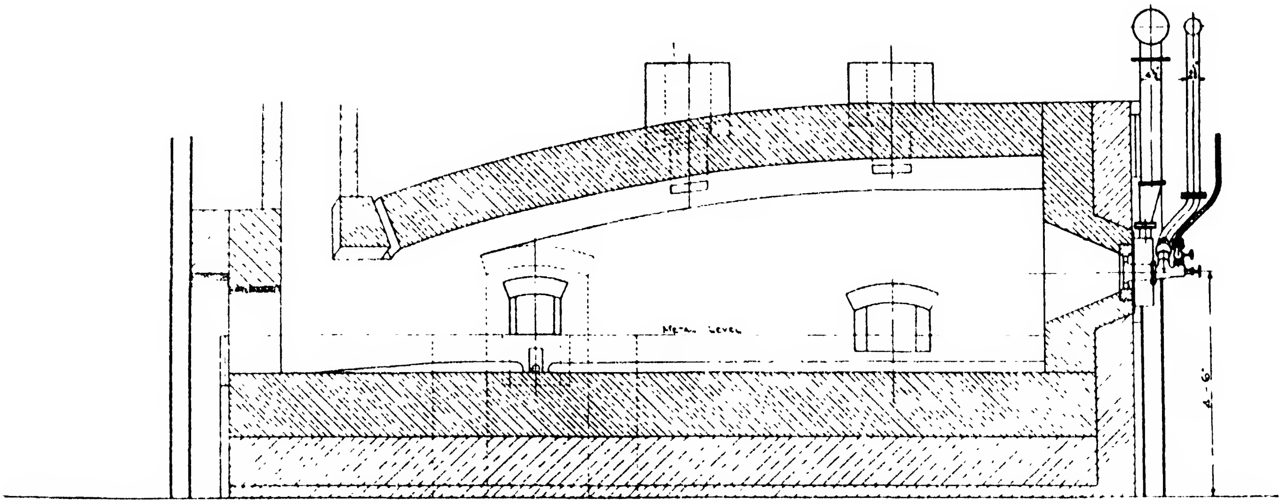


FIG. 33.

the ore is burnt into a form of clinker which can be passed to the blast furnace, in the case of iron ores, or the distillation furnace for zinc ores. The furnace operates on the down-draught principle, and all the air for combustion is passed through the low-pressure air burner.

(iii) Metal Melting.

(*a*) **Crucible.** Metal melting in crucibles represents one of the earliest and most successful applications of oil fuel. The metals include brass, copper, gunmetal, bronzes, aluminium, lead, cast iron, and nickel.

The arrangement normally employed is an oil burner usually of the low air pressure type firing into the annular space surrounding a plumbago crucible. In the case of aluminium and lead this crucible is sometimes of cast iron.

Typical results on a furnace of this type are given in Tables II and III below.

Another development of interest in the same sphere is the bale-out furnace for melting and maintaining aluminium chiefly in conjunction with the die-casting industry. The operating results give an oil consumption of approximately 5 kg. per hour to maintain 150 kg. of aluminium at casting temperature. When melting aluminium at the rate of 150 kg. per hour, the consumption would average 12 kg. of oil per 100 kg. of metal.

TABLE II

Brass, Gunmetal, and Copper

Number of melt	*Lighted up. H. M.*	*Shut down. H. M.*	*Duration of heat. Minutes*	*Oil consumption*		*Nature of charge*	*Wt. of charge. lb.*	*Final wt. lb. + or −*	*Metal loss*	
				Gallons	*lb. per 100 lb. of metal*				*lb.*	*%*
Heating up	8 57	9 27	30	3·5	..	..	..	..	..	..
1	9 42	11 20	98	10·75	8·61	Brass ingots Cu—60% Zn—40%	1,120	- 11	7·75*	0·692
2	11 34	12 47	73	8·25	6·62	,, ,,	1,120	−8	7·75*	0·692
3	1 10	2 27	77	8·5	6·82	Gunmetal ingots Cu—88% Sn—10% Zn—2%	1,120	−12	2·325*	0·2075
4	2 43	4 29	106	11·75	9·42	Copper ingots	1,120	+13 3/16	Negligible	

TABLE III

Aluminium

Heating up	9 23	9 56	33	3·75	..	..	..	..	..	..
1	10 3	11 5	62	6·5	15·6	Aluminium ingots	375	−4·25	4·25	1·133
2	11 22	12 9	47	5·0	11·98	,, ,,	375	−4·25	4·25	1·133
3	12 18	12 57	39	4·25	10·18	Aluminium scrap†	375	−24	24	6·4†

* Figures marked thus were calculated.

† The scrap was very oily and dirty, and many pieces were thickly painted.

In connexion with Table II, some metal from the first three tests was taken up by the copper of the final melt, which explains the apparent increase in weight.

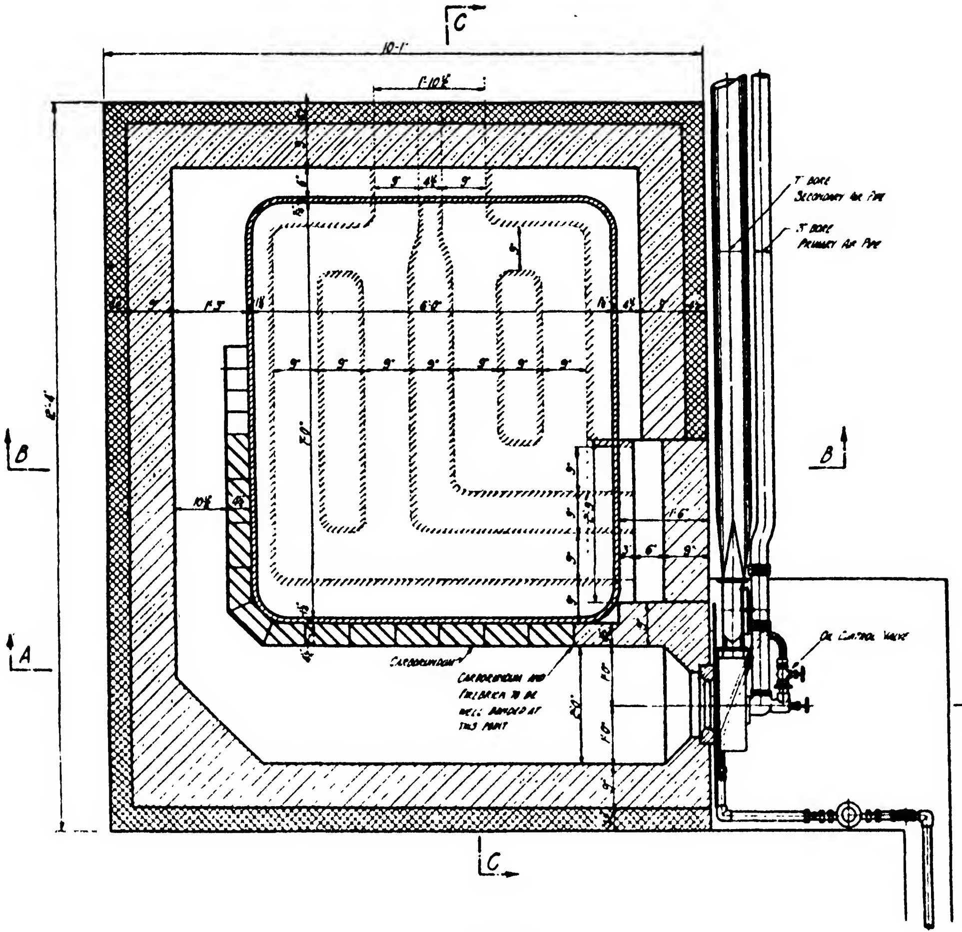


Fig. 34.

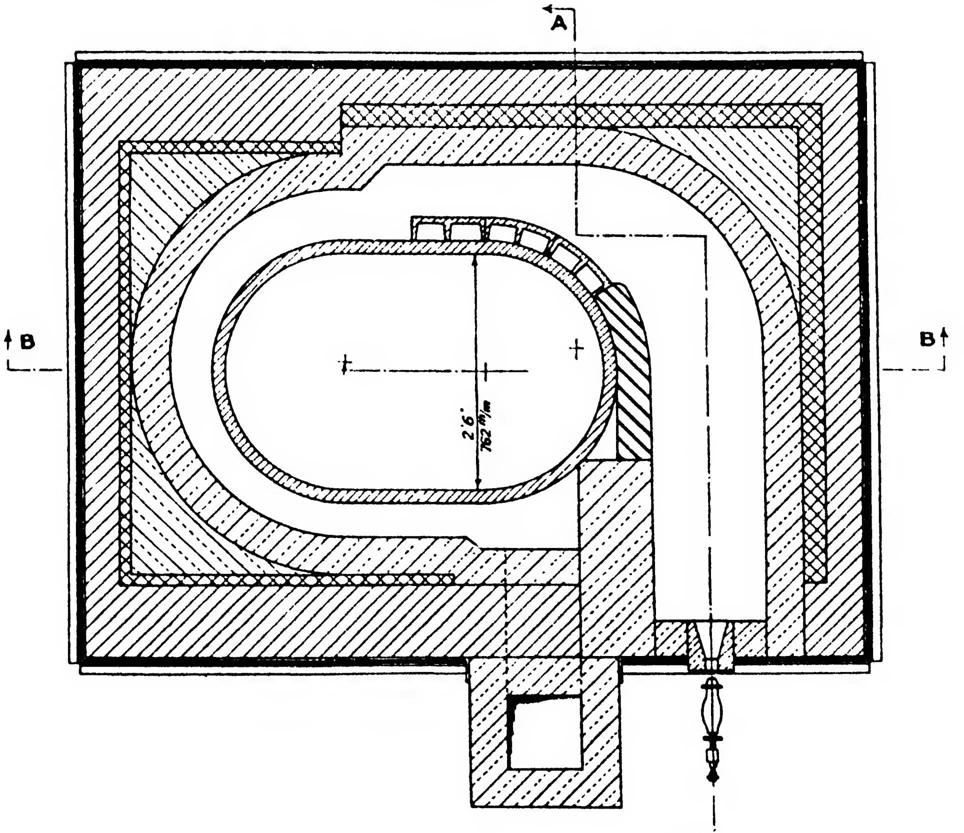


Fig. 35.

Galvanizing-bath furnaces.

Results for melting other metals in crucibles are approximately as follows:

Lead	1% weight oil to metal melted.
Brass, gunmetal, &c.	6% to 10% weight oil to metal melted.
Aluminium	10% to 12% " "
Cast iron	40% to 50% " "
Nickel	90% " "

(*b*) **Open Hearth, Rotary, and Semi-rotary.** Oil firing has been applied to open hearth steel melting furnaces, and for melting comparatively small charges of steel or iron, oil-fired rotary furnaces are in common use. Due to the speed of working, several melts can be obtained per day, and if required different metals can be dealt with during the same day. With the oil-fired rotary furnace high metal temperatures are possible, thus simplifying the casting of intricate parts. In one case, charges of special cast iron were melted in from 1¼ to 1½ hours, the metal being cast at temperatures of 1,560° C. to 1,600° C. with an oil consumption of between 14% to 17% of the weight of charge. When used for superheating molten metal, tests gave oil consumptions from 4½% to 8% of the weight of the charge and temperatures as high as 1,650° C. A full account of the operation of cast-iron furnaces is given by Faulkner [1].

Small open hearth furnaces are used for melting both ferrous and non-ferrous metals. A recuperator is fitted in the furnace flue and preheated air is delivered to a low-pressure air burner arranged to pass all the air required.

When used for melting aluminium an oil consumption of approximately 6% of the weight of the charge is obtained. For gunmetals a similar consumption figure is possible. This type of furnace is easy to handle, and gives very quick melting and low fuel consumption.

(iv) Welding, Forging, and Bending.

This important series of operations is carried out in a number of industries by means of the box type of direct oil-fired furnace. To obtain the temperatures usually associated with welding steel, fairly large metallic recuperators are fitted to give an air preheat of 200° C. to 400° C. Higher preheats can, of course, be obtained, but this would necessitate refractory recuperators.

Oil-fired welding furnaces are used in the manufacture of steel pipes and conduit, railway material, chain links, and similar parts.

A wide variety of forging processes lend themselves to the use of oil fuel. The smaller types of furnaces are used for such processes as rivet heating, nut and bolt making, drop forging, and for general smith-shop work. Larger furnaces are required for heating plates, bars, angles, pipes, &c., in boiler works and shipyards.

The oil consumptions obtained depend very considerably on the temperatures and method of operation of the furnace. For most forging work at temperatures up to approximately 1,000° C., with non-recuperative furnaces, about 10% of oil to weight of metal heated would be used. With recuperative furnaces it is possible to obtain consumptions as low as 6% for 900° C. to 1,000° C. down to 3% or less for temperatures not exceeding 600° C.

(v) Heat Treatment.

(*a*) **General Furnaces.** The intermittently fired muffle or semi-muffle is used freely at motor-car works and similar factories, and these are readily fired by oil burners.

Continuous furnaces are being increasingly used for this class of work. These again are readily fitted with oil burners which are also capable of being controlled automatically in accordance with the temperature required.

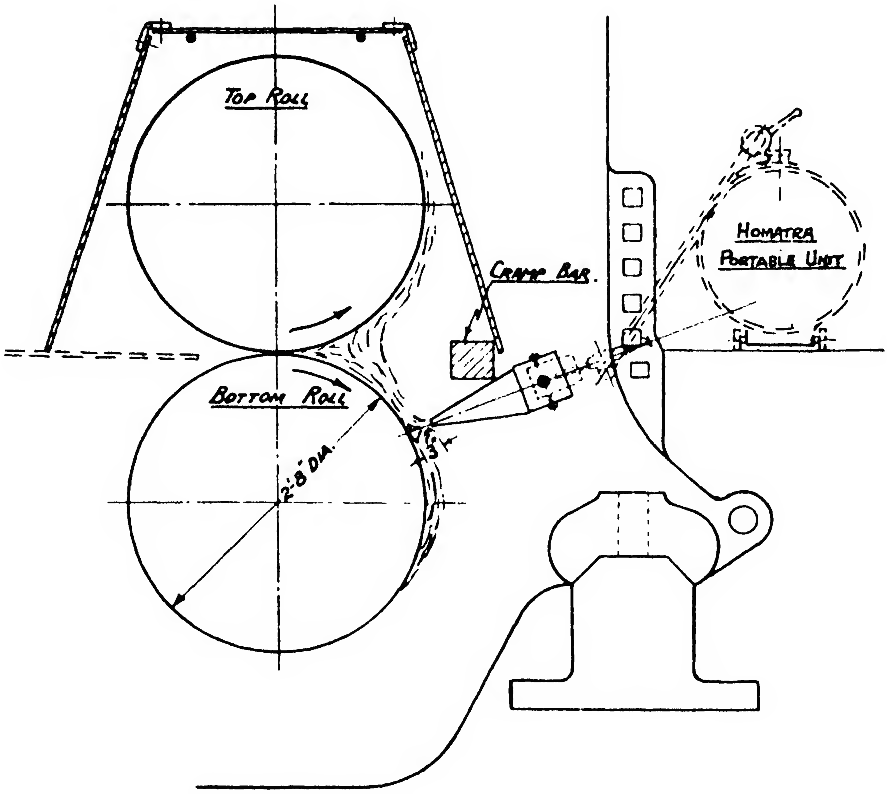


Fig. 36.

(*b*) **Salt Baths.** Salt-bath furnaces are particularly successful in connexion with 'Y' metal and other special alloys for the aeroplane industry. Test figures on a small bath of this type gave an oil consumption of 58 gallons against a previous town gas consumption of 17,400 cu. ft. for the same duty.

(vi) Galvanizing and Tinning.

(*a*) **Galvanizing.** The latest arrangement of a furnace for the continuous sheet galvanizing bath is shown in Fig. 34. It will be seen that a single burner is now employed instead of two firing opposite to each other at one end of the bath, which was the common practice till recently. In addition, the gases are taken under the galvanizing bath at the end of their travel, and this has not proved detrimental in respect to dross disturbance. To prevent burning out of the bath proportional protection has been applied along the sides, while in addition the flue gas passages have been designed to give approximately the same heat transference coefficient at every stage.

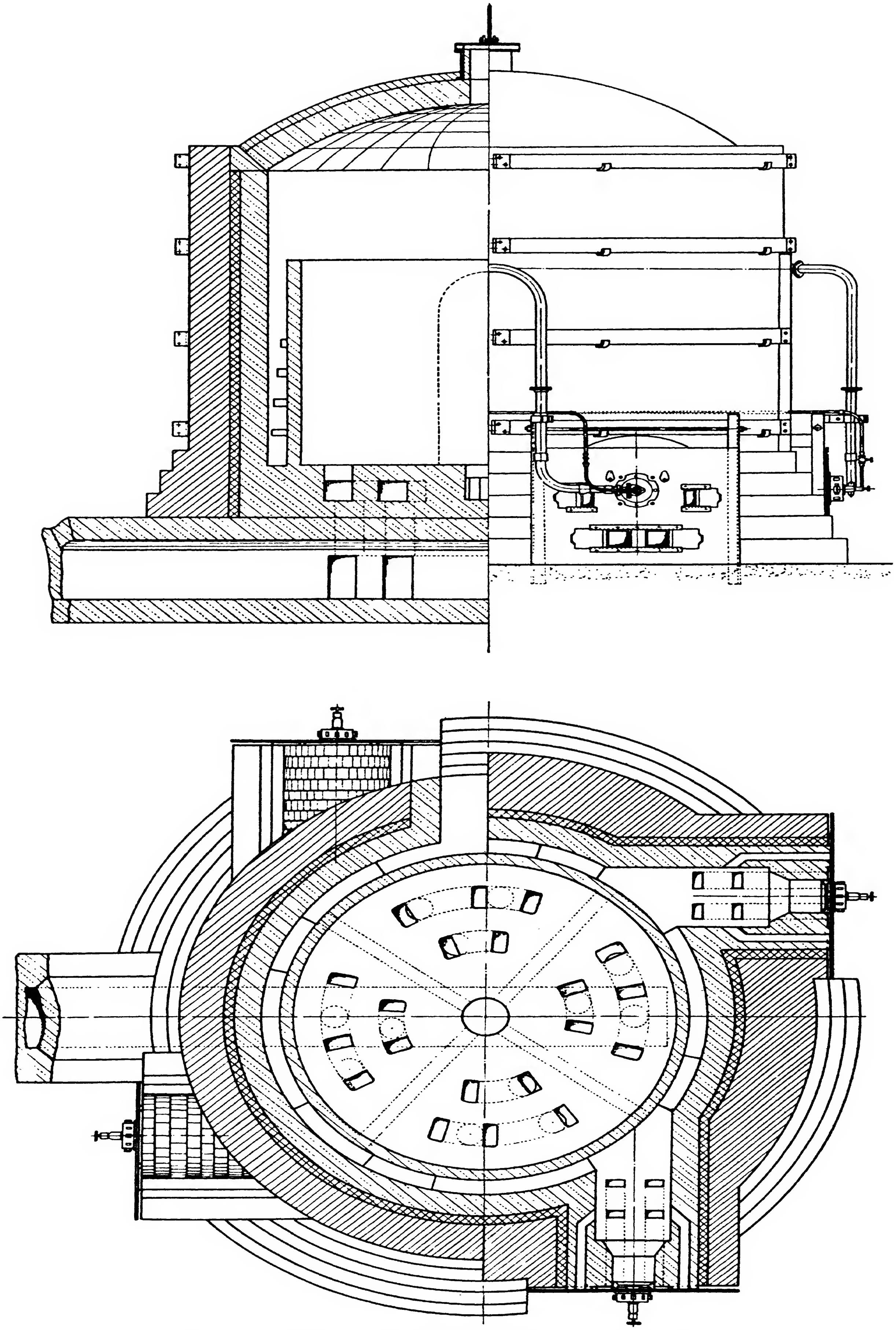


FIG. 37. Oil-fired circular down-draught pottery kiln

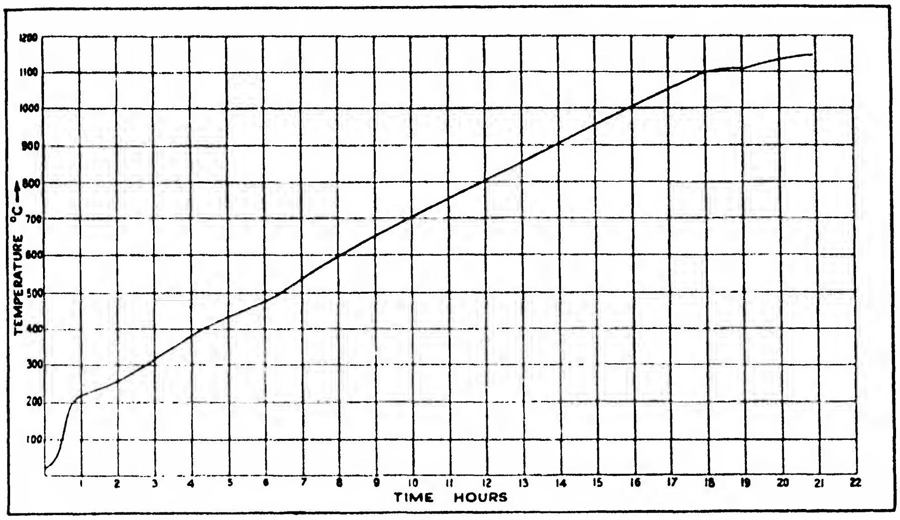


FIG. 38. Typical time-temperature curve for oil-fired pottery kiln.

The oil consumption depends upon the gauge of sheet and the rate of throughput, but an average figure is 40 lb. of oil per ton of sheet.

An arrangement of oil firing for a small dipping galvanizing bath is shown in Fig. 35. The oil consumption is 0·33 tons per week for an output of 6 to 7 cwt. per day of 8 hours. The bath life is 2 years against 2 to 6 months with coke.

(*b*) **Tinning Furnaces.** Oil fuel has been successfully applied to tinpot furnaces for the manufacture of tinplate. An average oil consumption of 1·8 lb. per box has been obtained at a works where the previous figure was 4·52 lb. of coal per box.

(vii) Roll Heating.

An interesting application of oil burners is the heating of sheet rolls preparatory to operations after the week-end shut down. This is carried out in a number of works, utilizing the open flame type of medium air pressure burner. Fig. 36 shows how this work is carried out. On a 6-hour shift for one set of rolls the oil consumption was approximately 36 gallons.

III. GENERAL INDUSTRIAL USES

1. Pottery Kilns

There are many different types of pottery kilns, some working on the batch or intermittent output, others on continuous production. The gas flow can be either up-draught or down-draught. Practically without exception all these kilns can be satisfactorily oil fired. The rate of temperature increase is very important in firing pottery ware, but, providing ordinary care is taken, any desired time-temperature curve can be obtained. It is also a simple matter to control the atmosphere inside the kiln.

Only the most common types of kilns will be considered here.

Circular down-draught kilns are employed in many works, and Fig. 37 shows a modern oil-fired kiln of this kind. There are four combustion chambers or fire-mouths placed tangentially and so arranged as to give a uniform distribution of heat inside the kiln. The products of combustion leave the combustion chambers and pass over the continuous bag-wall. A portion of the gases passes through ducts under the floor, entering the kiln through the centre 'well-hole'.

A time-temperature curve of the firing obtained on a kiln as described is shown in Fig. 38. It will be noticed how closely the temperature curve approaches the straight line required for this class of work.

The oil burners are of the low-pressure air type with natural draught air directors. Additional secondary air can be admitted through ducts as shown.

The firing of pottery ware is usually a slow 'cooking' process which can only be hastened to a limited extent. In certain cases, such as firing small electrical porcelain ware, comparatively rapid heating is employed, and oil shows to particular advantage under these conditions.

Muffle kilns are sometimes employed for glost or enamel firing. Providing the kiln is correctly designed and the muffle surface proportioned to the heat input rate, very even heating can be obtained throughout the charge.

For the production of large quantities of clay ware of uniform kind, continuous tunnel kilns are in common use. The goods to be fired are passed slowly through and are preheated and brought up to the firing temperature in the first half and slowly cooled during their passage through the second half of the tunnel. The direct or open fire tunnel kiln is the simplest form, but the muffle kiln is used for certain class of work.

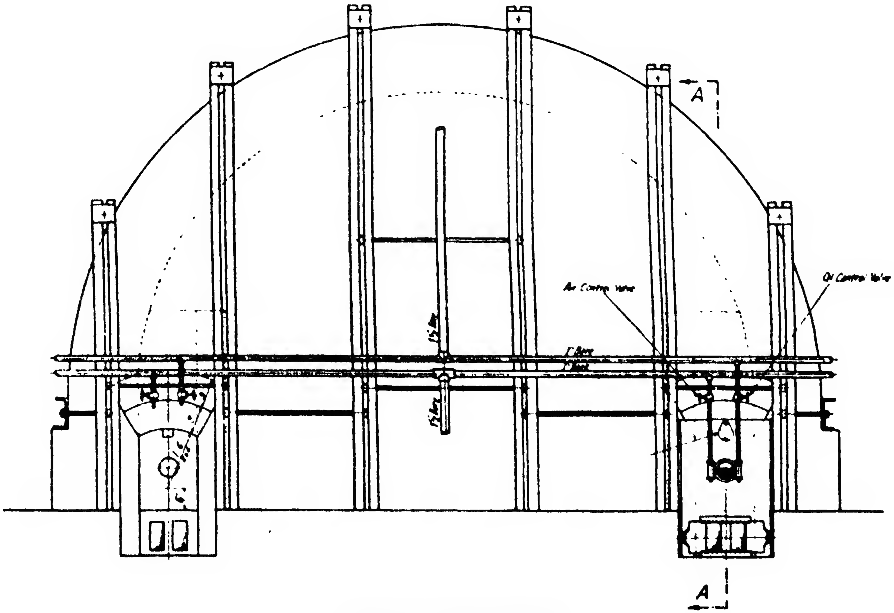


FIG. 39. End elevation.

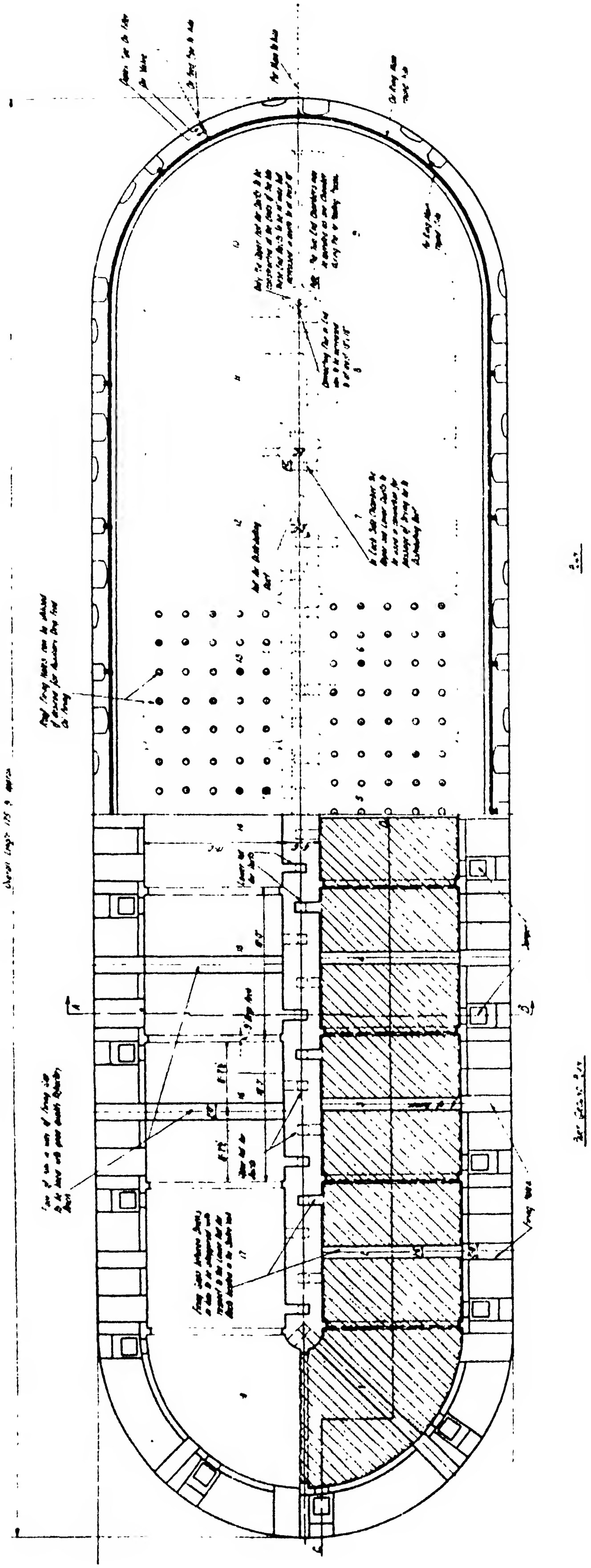


FIG. 40. Oil-fired continuous chamber brick kiln.

2. Brick Kilns

The firing of bricks and tiles is similar to firing pottery ware, and kilns of the intermittent or continuous type are employed. Fig. 39 shows a small rectangular kiln arranged for oil firing. This kiln would hold approximately 10,000 standard bricks. The burners are of the medium-pressure air type and must be so designed that they can operate over a large consumption range. During the initial stages of firing, the temperature must increase very slowly, which necessitates working the burners at very low individual rates of oil consumption. After the 'water smoking' period the consumption rate can be increased. Only a small amount of air is passed through the burner for atomizing purposes, the remaining air being admitted beneath the burner and into the combustion chamber through openings in the floor.

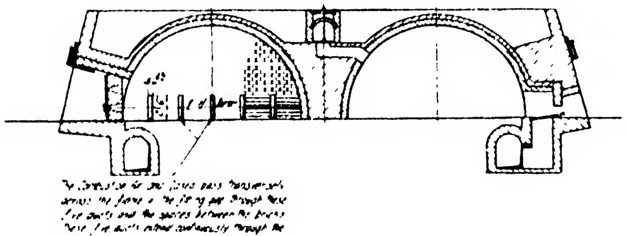


FIG. 41. Sectional elevation through firing hole and hot-air duct.

In addition to continuous kilns of the tunnel type, the continuous chamber or 'Hoffman' kiln can be oil fired in quite a simple manner, and Figs. 40 and 41 show such a kiln. Cold air is allowed to enter at a chamber where the bricks have already been fired. This air passes through the cooling bricks in two or three chambers, and thus becomes highly preheated. It is then available for combustion purposes in the chambers which are being fired. Advantage is taken of this highly preheated air, and the amount of cold air introduced through the burner is kept to a minimum. Burners of the medium-pressure air type are therefore employed. Referring to Fig. 40 it will be noticed that combustion chambers are formed between the stacks of bricks to be fired. The burner must be capable of throwing a flame the full length of the combustion chamber without impingement on the side walls. It is usual to employ, say, three or four burners per kiln, and these are moved from chamber to chamber as the firing proceeds round the kiln.

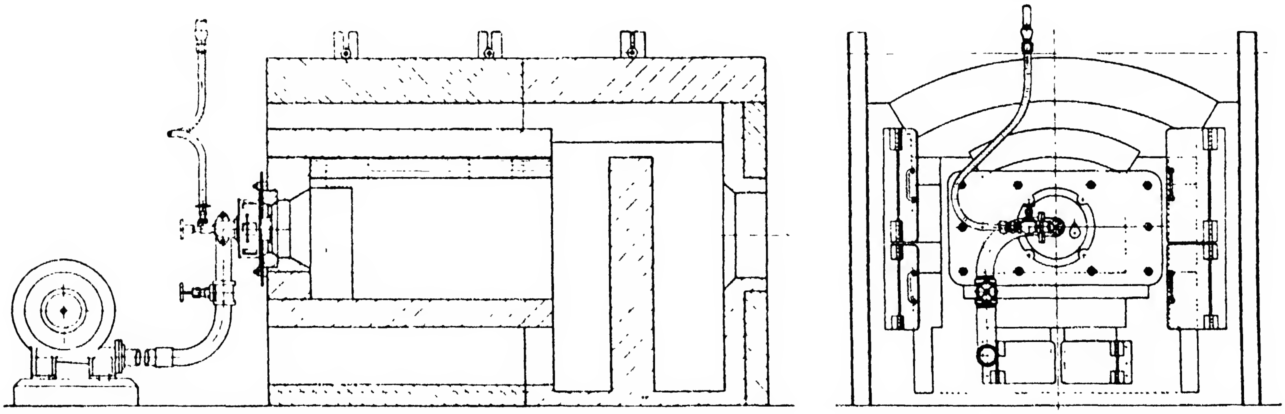


FIG. 42.

The oil consumption per 1,000 bricks depends on many factors, such as the type of clay employed, the firing temperature, and total firing time. In some cases coke breeze is mixed with the clay, and this reduces the amount of fuel required to fire the brick. On the whole an average figure would be from half to one-third the amount of coal for a similar brick on a similar type of kiln.

Certain classes of bricks have to be dried before they can be stacked in the kiln. At some works these bricks are dried in the open. A more modern method is to employ drying sheds which are heated with a mixture of air and the products of combustion from an oil-fired furnace. Fig. 42 shows the type of furnace used for this purpose. The combustion chamber is designed so that combustion can be completed before the gases mix with the cold air which enters along each side. This furnace is designed to supply 10,000 cu. ft. of air per minute heated to 200° F. on an oil consumption of 10 gallons per hour. For further details see Lubbock, 'Oil Fuel in the Brick Industry' [6].

3. Glass

For the production of standard shaped articles (e.g. bottles, jars, &c.) and also for plate glass, large tank furnaces are employed. Oil firing has made great headway in the glass industry, since the tanks can be operated at high rates of output. This reduces materially the initial capital outlay on the tank itself. In addition there is the further saving in both capital and maintenance charges due to the elimination of producers. With oil fuel it is possible to liberate in the furnace more B.Th.U. per cu. ft. of space than with producer gas. The volume above the glass can be reduced, which, in turn, reduces the amount of brickwork surface forming the side walls and hence the radiation losses. For large outputs and economical working it is usual to employ furnaces working on the regenerative principle. In this case the amount of cold air for atomizing the oil must be kept at a minimum, and medium air or high-pressure air burners are employed. In certain cases pressure-jet burners have been used, but burners of the air atomizing type appear to give greater satisfaction in service. It is only necessary to install one regenerator chamber on each side of the furnace as compared with two required with producer gas fired furnaces. When melting flint glass, rates as high as 1 ton of glass per 24 hours per 9 sq. ft. of melting end surface can be obtained. Tank furnaces have been operated at higher rates, but these are not usually maintained for long periods. It is possible to 'pull' 5 tons of molten flint glass per ton of oil burnt.

When the output of glass required is small, recuperative furnaces are employed. The recuperator can consist of loops of steel piping arranged in the furnace flue.

In accordance with the general principles of air preheating mentioned previously, refractory recuperators are used on glass tanks when the temperature conditions necessitate this.

The temperature of the preheated air on recuperative furnaces is usually lower than on regenerative furnaces. As a consequence, the flame temperatures are somewhat lower, the rates of output are not so high, and the oil consumption per ton of glass is greater.

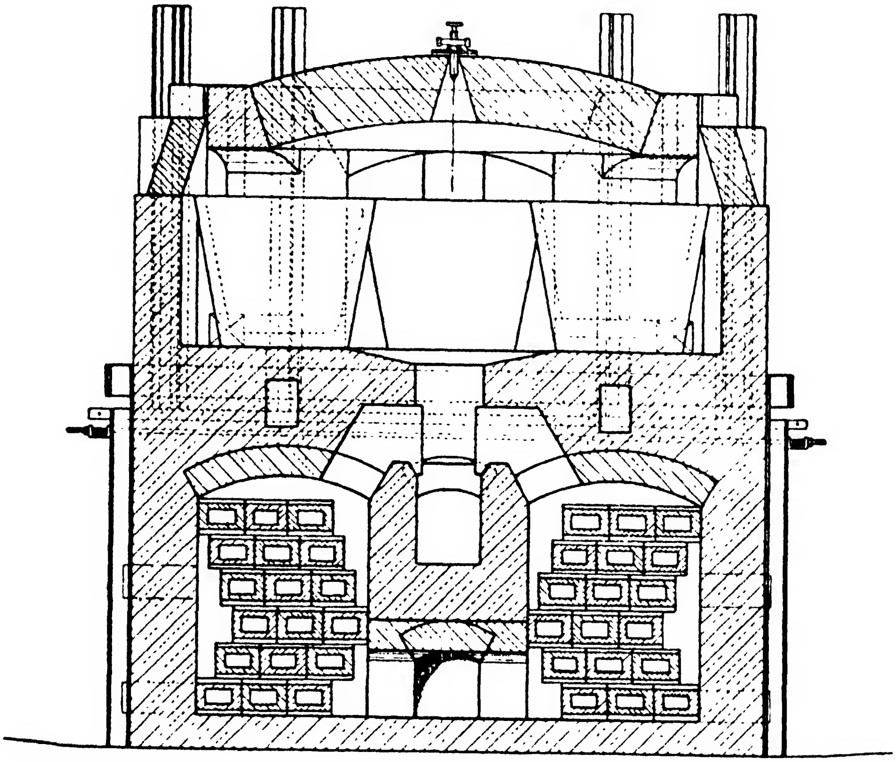


Fig. 43.

Pot furnaces are employed in the manufacture of special quality glass, and while the majority of the existing pot furnaces are fired with producer gas, great headway has recently been made in adapting oil firing for this type of furnace. Fig. 43 shows a 4-pot glass furnace with a burner of the medium-pressure air type arranged to fire down through the crown of the furnace towards the eye. Secondary air is preheated in the recuperator and enters the furnace through the eye, combustion taking place just above this point.

In addition to the various types of furnaces employed for melting glass the annealing lehrs are usually oil fired. The modern lehr has been improved by careful use of insulation and arrangements whereby the heat of the incoming glass ware is conserved to help in the annealing process. Tests on a series of large lehrs have given an oil consumption of 80 gallons per 24 hours for an output of 20 tons of glass.

4. Bread Baking

There are many different types of ovens employed for baking bread, but in the majority of cases oil fuel has been adopted with very satisfactory results. The amount of fuel required varies with the type of oven and the class of work, but for bread baking in steam-tube ovens of the draw-plate type 1½ to 2 gallons of oil per sack of flour (280 lb.) is a common figure.

Travelling or continuous ovens are usually more efficient, and figures of 1 gallon of oil per sack have been recorded. Fig. 44 is the rear view of a continuous oven, showing the oil burners and oil-firing equipment.

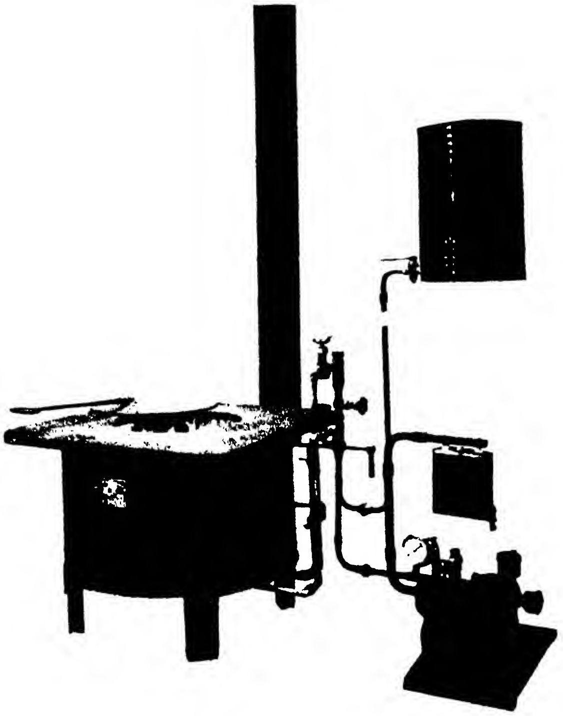
Ovens used for baking special biscuits and certain classes of cereal food are also oil fired. The oil consumption is approximately 9 gallons per hour for an output of 1,000 lb. of biscuits per hour.

5. Enamelling and Stoving

Vitreous enamelling is employed to an increasing extent in the manufacture of cast-iron baths, gas stoves, weighing-machine parts,&c. The enamelling is carried out in a muffle, and oil fuel is employed widely for this type of furnace. The burners used are of the low-pressure air type having a consumption range of from 8 to 14 gallons per hour. Secondary air is admitted through the director. The burner fires into a combustion chamber placed beneath the muffle so that the gases leave at the end of the combustion chamber and pass up the muffle on each side. The gases leave the furnace at the lowest point on each side of the muffle at the end opposite to the charging door. Muffles have to operate under very exacting conditions, and the advantages with oil are in the uniform temperature obtainable. In addition the absence of dust saves spoiling the enamel surfaces.

Stove enamelling or japanning requires an oven or stove in which the articles to be stoved can be placed and the varnishes dried on and hardened. Intermittent work can be carried out in small ovens which are supplied with heated air from an oil-fired air heater. In certain cases the oven can be heated directly by the products of combustion. For stoving standard articles, such as mudguards and the

FIG. 44. Continuous baking oven—rear view



406

Fig. 45. Oil-fired unit for sugar-boiling and jam-making

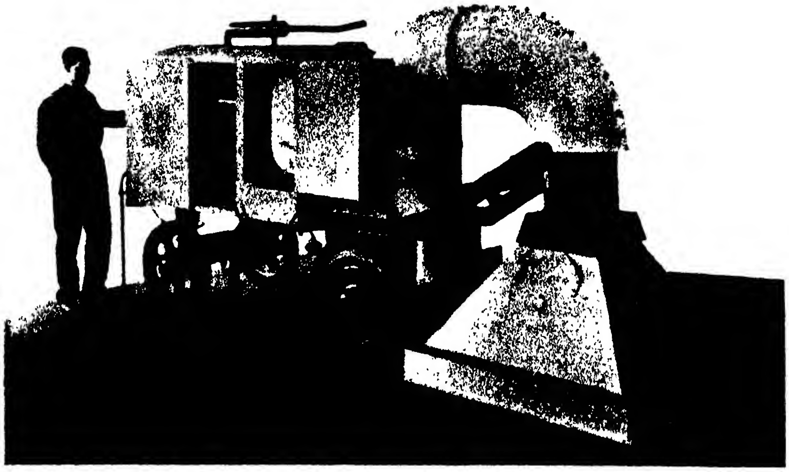


Fig. 47. Oil-fired road heater

wheels of motor-cars, oil-fired continuous ovens are usually employed, which are supplied with hot air from an oil-fired furnace. A stove of this type gave an output of 75 motor-car mudguards per hour on an oil consumption of 6½ gallons per hour.

Oil-fired furnaces are employed in the manufacture of the frit required for vitreous enamelling. Frit is used to form the gloss or enamel on the surface of metal parts, pottery, &c., and is made from various materials, such as flint, fluorspar, metallic oxides, &c., which are mixed together in the dry state and melted. Average figures obtained on a number of different furnaces give an oil consumption of 16% to 25% of the weight of the charge.

6. Pot Furnaces for Varnish, &c.

There are many different trades in which pot furnaces are employed, such as varnish manufacture, sugar boiling, jam making, &c., in which temperature control is of the utmost importance. A charge consisting of 675 lb. of linseed oil in a cast-iron pot weighing 420 lb. was raised from 40° F. to 600° F. in 70 minutes with an oil consumption of 4 gallons per hour. The pots are frequently removed from the setting and the furnace draught is broken. It is usual to employ low-pressure air or rotary burners. In the event of the varnish being overheated fires are liable to occur if the pot boils over. The ease with which the oil flame can be regulated enables the charge to be brought up to the correct temperature without risk of overheating, but should the operator allow the charge to become overheated and a fire occur the oil burner can be turned off by a remote control.

For sugar boiling and jam making small oil-fired units as shown in Fig. 45 are in common use.

A few typical results are:

Weight of charge	*Final temperature*	*Melting time*	*Oil consumption*
60 lb. sugar glucose .	320° F.	20 min.	2 gall. per hr.
56 lb. sugar . . .	320° F.	19 min.	2 gall. per hr.

In another case a pot having a capacity of 22 gallons was converted to oil firing. The melting time with gas was 75 minutes and with oil fuel 15 minutes.

7. Rotary Kilns

(*a*) **Portland Cement.** Cement is usually produced in rotary kilns which can be satisfactorily fired by oil fuel. Different oil-burning systems are used, such as a single large locomotive type of steam-jet burner, one or more compressed-air burners, a single pressure-jet nozzle, and recently one large low air pressure burner.

The oil consumption for a given weight of clinker varies considerably with the process used, the type of cement burnt, and the size of kiln. The direct fuel consumption is usually equivalent, on a B.Th.U. basis, to the coal figure for the same kiln and cement. Large savings in other directions can be obtained by lower initial capital cost and by the elimination of coal handling, drying, and pulverizing.

(*b*) **Sand Drying.** Fig. 46 shows the arrangement of an oil-fired sand dryer, the sand being used in the mnaufacture of facing tiles and bricks. The burner used in this case is of the rotary type. For an output of 20 tons of sand per 8-hour day the oil consumption is 60 gallons.

8. Vertical Kilns

Vertical kilns are used in the manufacture of cement, lime, hard plaster, &c. In such kilns care must be taken to ensure that the material charged is not so small as to impede the free flow of the products of combustion or so large that the centre of the lump remains unburnt. The gypsum is heated to a temperature of 1,200° F. (650° C.) and an output of 60 tons per 132 hours with a corresponding fuel consumption of 92 lb. of oil per ton has been obtained.

9. Crematoria

The chief requirements for the design of a crematorium furnace are as follows:

(*a*) The furnace should be capable of being heated rapidly to a temperature of about 2,000° F.
(*b*) The cremation should be carried out as quickly as possible and without formation of smoke.
(*c*) Easy access for the removal of ashes must be arranged.

The fuel consumption on different types of furnaces varies from 12 to 25 gallons per cremation, depending to a great extent on the interval between successive cremations.

10. Air Heaters

Many drying processes are carried out with hot air supplied from oil-fired air heaters. For tea drying, sectional air heaters are frequently used, and these can be readily oil fired. For heating 2,000 cu. ft. of air per minute from 60° F. to 570° F. an oil consumption of approximately 8½ gallons per hour is required.

11. Road Making

(i) **Macadam Plants.** There are many types of plants used in the preparation of road material, most of which are self-contained travelling units. The central portion of such a plant consists of a rotating drum into which is fed stone, sand, and other materials. A supply of bitumen or tar at the proper temperature is added to the materials at a later stage. These rotary drum plants fall generally into two categories, i.e. either they are externally heated from a box-shaped furnace under the drum, the gases being drawn subsequently through the drum itself, or the rotating drum is directly fired along the axis.

The advantages of oil fuel for this class of work lie in the fact that road material can be prepared as and when required. Consumption figures vary widely according to the class of material, the percentage of moisture, and the temperature. With stone and sand which are worked at high temperatures of about 350° F. the oil consumption is between 0·8% and 1·4% by weight of the dried material.

The low-temperature plants now in use for bituminous macadam operate with the material brought up to 150° F. instead of 350° F. The oil consumption is therefore much lower, an average figure being 0·2%.

(ii) **Road Patching and Melting.** Portable oil-fired plants are now being used for melting patches of asphalt road surface, so that new aggregate can be rolled in while the surface is plastic. In some cases melting to a shallow depth is merely used for imparting a non-skid surface, by raking over the softened sections with steel wire brushes or similar appliances.

The actual heater is arranged either with a horizontal or vertical burner. In the latter case the flame is projected

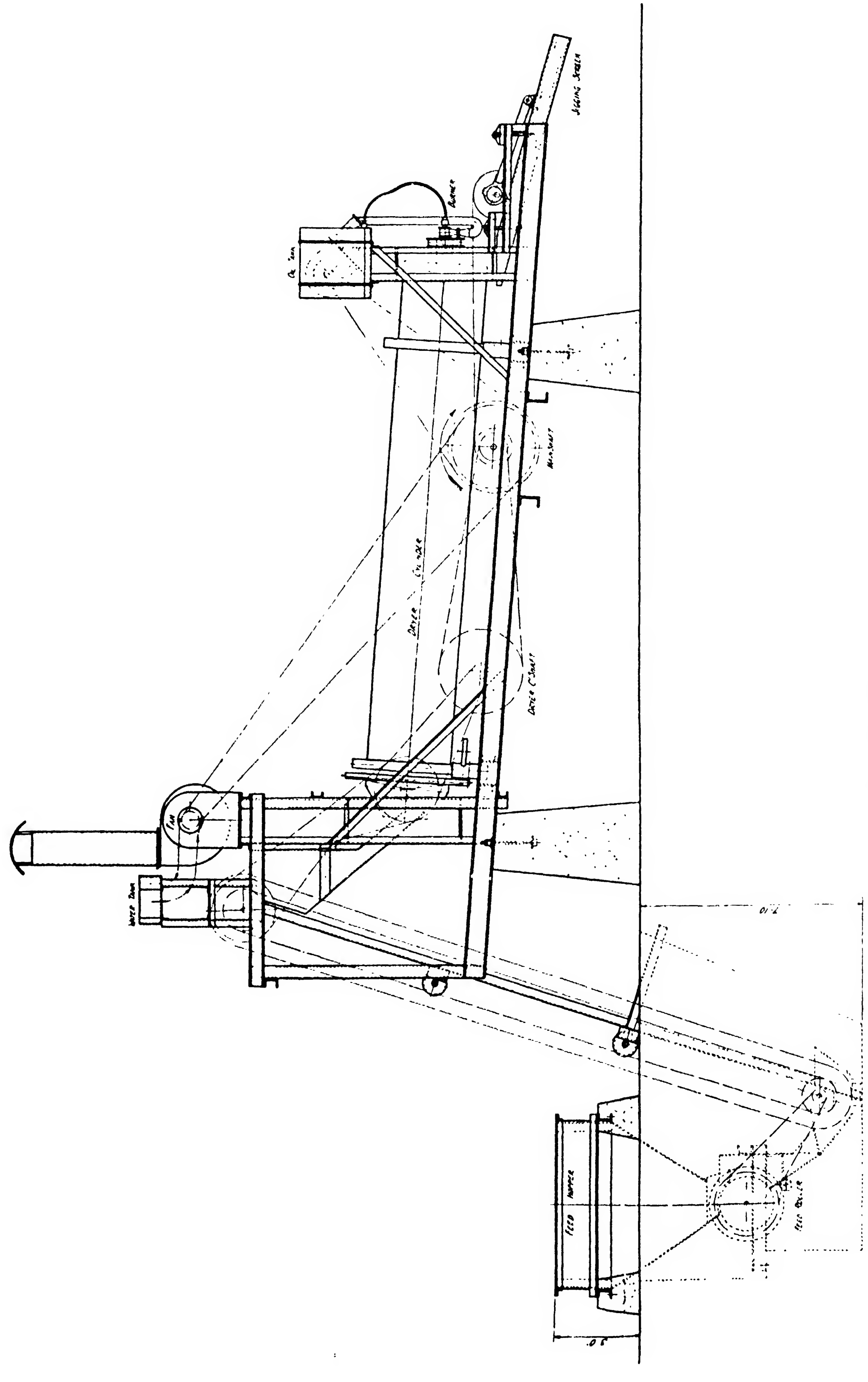


Fig. 46. Oil-fired sand dryer.

downwards from the apex of a hollow box, approximately in the form of a trapezium. In addition to an air compressor or high-pressure fan for atomizing purposes, a low-pressure or 'volume' air fan is fitted so that it is possible to obtain any required gas temperature at the road surface. The desideratum does not consist so much in having extremely hot gas reaching the road, as a comparatively large volume of gas at 500° F. to 1,000° F. according to the class of work involved. The area at the base of these appliances is of the order of 6 ft. by 6 ft., or on small machines 4 ft. by 4ft., so that fairly large patches of road can be dealt with rapidly. Fig. 47 is an illustration of one of these heaters fitted with Laidlaw Drew oil burners.

12. Gas Enriching

The principles of operation of gas-enriching plants are well understood. The usual enrichment of water gas from 300 B.Th.U. per cu. ft. to 500 B.Th.U. per cu. ft. is obtained with approximately 1·5 gallons of oil per 1,000 cu. ft. of finished gas, the increase in volume being approximately 12% based on the final volume produced. An average analysis of enriched gas is as follows:

Hydrogen	37·0%
Methane	15·0%
Hydrocarbons	7·0%
Carbon monoxide	30·0%
Carbon dioxide	5·5%
Nitrogen	5·5%

REFERENCES

1. Faulkner, V. C. *Foundry Trade Journal,* 26 Oct. 1933.
2. Gollin, G. J. Fuel Oil for Central Heating. *Heating and Ventilating Magazine,* **4** (1931).
3. Haslam, R. T., and Russell, R. P. *Fuels and Their Combustion* (1926).
4. Lubbock, I. The Storage, Handling and Transmission of Liquid Fuel by the User. *Transactions World Power Conference* **1,** 7–9 (1928).
5. Lubbock, I. Industrial Uses of Fuel Oil. *J. Inst. Fuel,* **4,** no. 14 (Dec. 1930).
6. —— Oil Fuel in the Brick Industry. *Trans. Ceramic Soc.,* Feb. 1931 and Nov. 1932.
7. Romp, Ir. H. A. *Oil Burning.* (In English) Martinus Nijhof, The Hague.
8. Spiers, H. M. *Technical Data on Fuel* (1932).
9. Tapp, H. F. *Handbook of Domestic Oil Heating.* American Oil Burning Association, New York.

UTILIZATION OF FUEL OILS FOR STEAM-RAISING PURPOSES

By J. S. S. BRAME, C.B.E., F.I.C., F.C.S.
Alexander Duckham & Co., Ltd., London

ALTHOUGH oil was obtained on a small scale centuries ago, and in Burma in considerable quantities, by primitive methods, the 'oil age' is generally regarded as commencing with Colonel Drake's discovery at Oil Creek in 1859. But a few years later attempts to use the heavier residues for fuel were made, then Simm and Barff (1865–7) carried out extensive trials and Dorsett (1868–9) endeavoured, with but little success, to use heavy oil by gasification in a chamber external to the furnace proper.

Some of the pioneer work in utilizing oil as fuel was carried out in Russia, where the first oil monopoly was granted in 1872.

In the early days of the industry kerosine was the all-important product, and after topping off the fractions which could be used for its production a considerable volume of heavy residue, often as much as 60% of the crude, remained, and it was a natural outlet for this to be used as a fuel; at first in producing countries.

Naturally the adoption of liquid fuel in countries where importation was involved was not so general, but for marine purposes the outstanding advantages of liquid fuel over coal for boiler use have led to its almost universal adoption for naval vessels and in the larger vessels of the mercantile marine. So much has this been the case that some of the largest liners built for coal burning were converted to oil firing at a cost of many thousands of pounds. The first entirely oil-burning destroyer of the Royal Navy was introduced in 1907; the first all-oil battleship was the *Queen Elizabeth* (1918).

For railway use, as would be natural, the oil-producing countries were pioneers, and in some, like Mexico, where imported coal fuel was used the discovery of oil led to its complete replacement by oil fuel. Although at the time of coal strikes oil-fuel fired locomotives have been temporarily adopted in this country, its use for this purpose is exceptional. It is worthy of record, however, that, owing to the enthusiasm of Mr. Holden, and the favourable price of tars and tar oils, there were 80 locomotives, out of 1,200, operating on the Great Eastern Railway in 1903, but the number had fallen to 6 only by 1909.

In some cases oil was burnt in conjunction with coal, and the following comparative results were recorded. Per mile, coal 11 lb. plus oil 12·2 lb., total 23·2 lb; 9 other coal-burning engines on the same route averaged 34 lb. coal. According to A. F. Bailey [1, 1921], a locomotive operating the passenger train service between London and Birmingham had an oil consumption of less than 1 gallon per 100 ton miles.

Alarm is not infrequently expressed at the growing use of oil fuel in place of coal in this country, but in fact the actual replacement need not cause apprehension. Approximately 75 million tons of coal are used annually for power production, whilst the heavy fuel oil imported and home refined from crude oil is but little over three million tons, and of this over 50% is used as ships' bunker oil. According to the *Oil News* (11 May 1933) the following are the quantities used in the several industries:

Consumption of Fuel Oil (1933)

Ships' bunkers (including naval) . . .	1,575,000 tons
Metal trades and glass	375,000 ,,
Central heating (public and private) . .	205,000 ,,
Steam (industrial)	90,000 ,,
,, (public buildings)	80,000 ,,
Other uses	600,000 ,,
	2,925,000 tons

It is difficult to assess this oil consumption in terms of coal, on account of an unknown proportion being used as fuel for compression-ignition engines, but assuming on an average that 1 ton of oil is equivalent to 1·75 tons of coal, the coal equivalent is about 5½ million tons.

Advantages of oil compared with coal are as follows:

1. Higher calorific value 19,000–19,500 oil—12,500 coal.
2. Better stowage value—average for oil, about 38 cu. ft. per ton; coal, about 43 cu. ft.—which taking into account the relative calorific value gives, approximately, an advantage to oil of 1·74/1 per unit of stowage space.
3. Owing to maintenance of steady combustion conditions there are not the losses of sensible heat units as with coal fires, particularly with hand firing. Consequently, a higher evaporation efficiency is attained than that merely arising from the higher calorific value.

In the case of the *Aquitania* with coal firing, 28 out of 168 furnaces were cleaned every watch, the approximate loss of heat units per 24 hours being estimated to be equivalent to 8,000 h.p.

4. Absence of non-combustible matter (ash and moisture). Consequently, disposal of ashes, with accompanying dirt and dust, is obviated (a factor of importance particularly in marine work).
5. Handling of fuel oil, entirely by pumping, reduces labour to a minimum. Because of its mobility the delivery of fuel oil is much more expeditious; in emergency it is possible to pump from a tanker into the oil tanks of a warship. The dirt entailed in coaling is overcome.
6. Coal bunkers have to be suitably placed to discharge conveniently for firing. On the other hand, oil tanks may be situated in any convenient position; on shore, underground, thus saving space; on board ship, in fore and aft compartments or in the double bottoms. Much valuable cargo space may thus be rendered available.
7. Reduction of boiler-room staff follows on several of the above-mentioned advantages.

Available Liquid Fuels. Apart from questions of cost, fuels from the following sources are available; petroleum, shale oil, tars and tar oils from the carbonization of coal, tars from water-gas plants, and tars from producer-gas plants using bituminous coal. The two latter are used only as an economic means of disposal. Coal tar and tar oils have practically gone out of use, better use can be made of them in other ways, and the demand for road tar, pitch, &c., has caused such an advance in price that their use as fuel for burning is seldom warranted. In 1909 the value of tar was 10*s.* 9*d.* to 14*s.* 9*d.* per ton; by 1913 it had risen to 28*s.* 6*d.*

to 33*s*.; at the end of 1934 it was 25*s*. to 28*s*. The development of large-scale hydrogenation of tar oils and low temperature tars, for the production of motor fuel, with the other factors mentioned, will make the future use of tars as boiler fuel oil quite uneconomical.

At one time the heavier portions of shale oil were used as fuel oil for burning. They were of much higher grade than the usual residue fuel oils from petroleum, being practically free from asphalt. Since the rapid development of the compression-ignition engine the advantages of shale oil are such that the use for steam raising is quite uneconomical. Moreover, the production in recent years has very considerably declined.

Petroleum Fuel Oils. Since the practically universal requirement that fuel oil shall have a closed flash-point not below 150° F., the available oils from this source are residue oils. Further, since the residue oils from the higher-grade crude oils yield more valuable products in the form of Diesel oils, gas oils, lubricating oils, and often paraffin wax, broadly speaking it is from the more asphaltic types of oil that the fuel oils are produced.

Before fuels of high vapour pressure were in demand for internal-combustion engines large quantities of crude oil were left exposed to the sun and wind to evaporate off the then valueless lighter components, the residue constituting 'fuel oil'. The process was known as 'sunning'.

Later the recovery of these lighter fractions was achieved by the simple distillation process of 'topping'. Details of the current practice in the distillation of crude oils are dealt with elsewhere, to which reference should be made. Here it will only be necessary to consider the requirements of fuel oil, and these are very few, since almost any residue may be burnt, and it becomes therefore largely a question of the requirements to render their use free from fire and explosion risks.

Flash-point. As previously mentioned, for purposes other than use in warships the closed flash-point is almost universally accepted as not below 150° F.

For naval use a higher flash-point has been regarded as necessary, but experience has gradually enabled the flash-point to be reduced to 175° F. with the exception that for the more fluid oils the figure of 200° F. is laid down.

Viscosity. This is of primary importance from the point of view of handling by pumps, since from the burning aspect the viscosity may be satisfactorily reduced by the preliminary heating just prior to use.

Largely the viscosity is determined by the asphalt content.

For the more viscous oils the standard Redwood and Saybolt viscometers had too slow a period of flow, and their design was accordingly modified to increase it in special fuel-oil patterns to ten times the rate. To-day, therefore, the viscosity is measured in the Redwood II (I.P.T. Serial Designation LO. 8) and Saybolt 'Furol' instruments (A.S.T.M. Serial Designation E.D. 88–33).

Little else is required beyond that the fuel oil shall be reasonably free from water and adventitious matter, which would lead to unduly rapid clogging of the filters in the system, or, escaping these, the blocking of the orifices of the sprayers. The calorific value is amply covered by the general requirement that the oil shall be wholly of petroleum origin.

For marine use it is usual to specify a limit for the sulphur content. At one time it was thought the sulphur gave rise to corrosion in the uptakes, funnels, &c., but the real objection is the high percentage of sulphur dioxide in the funnel gas. In passenger steamships this, under certain conditions, made the atmosphere of promenade decks most unpleasant; in naval vessels the fighting tops, &c., became untenable. The Admiralty requirement limits the sulphur to 1·5%.

American specifications have been issued for several grades of fuel oil, but two only are of importance for steam-raising purposes; these are as follows:

Class	*Flash-point (minimum)*	*Water and sediment (max.)*	*Viscosity Saybolt 'Furol' (max.)*
Bunker B	150° F.	1·0%	100 sec. (122° F.)
Bunker C	150° F.	Water 1·75% Sediment 0·25%	300 sec. (122° F.)

The Burning of Fuel Oil

The ideal for perfect combustion would be the preliminary conversion of the liquid into vapour, and although this is practicable with light oils, for those heavier oils now employed all such systems are impracticable, on account of cracking and carbon formation in the vaporizers.

The next finest state of subdivision is in the form of a mist or spray, easily ignitable with air, so that combustion is almost perfect. The spraying of the oil is frequently referred to as 'atomization', a term perhaps expressive, but open to scientific criticism. In steam raising conditions are less favourable to perfect combustion than in the case of ordinary furnace heating, where the high wall temperatures are favourable to perfect combustion, even with a fairly coarse spray. The big temperature difference between the plates or tubes in a boiler and the flame tend to check combustion unless it is nearly or quite completed before the flame reaches cool surfaces, and bad smoke will result. This is especially the case when lighting up.

Three systems of spraying or atomizing are in use—air, steam, and mechanical spraying. The first-named is used in steam practice only for small boilers, such as those used for starting up the main plant, and in 'donkey' boilers for marine purposes. Statements vary on the relative efficiency of the air, steam, and pressure systems; much depends, naturally, on the design of the units. According to Kermode the efficiencies are: air, 78–83; steam, 68–74; pressure, 70–75%; whilst A. F. Baillie [1, 1921] gives 80 (air), 78 (steam), and 85% (pressure).

Steam Sprayers. These have been very widely used and present special advantages such as simplicity of outlay and minimum space occupied. The spraying agent is also available in adequate amount and at any required pressure once steam has been raised. With many earlier types of sprayers the steam was allowed to jacket the oil supply and help in heating up the oil.

For locomotive work steam atomization has the definite advantage of economy of space, due to simplicity.

Drawbacks to the use of steam are: (1) the considerable loss of water as steam in the flue gases, (2) the necessity for some small auxiliary supply for starting-up purposes.

Since in general the steam is taken off from the main supply, reliable data on its consumption is difficult to obtain, but from the extensive series of tests made by the U.S. Navy Fuel Board, using a small independent boiler, the average requirement was 0·6 lb. per lb. of oil. The steam lost is equivalent to about 4–5% on the total generated. This loss is not serious in most cases of shore practice, but for marine purposes has definitely ruled steam spraying out since the introduction of marine boilers for the 'make-up' of which evaporators have to be employed.

Extravagant claims were at one time made for steam as materially assisting the combustion process, but as steam is one of the most efficient methods of extinguishing oil fires, it is impossible to reconcile this with any helpful action in combustion. In fact steam displaces valuable air, and one effect definitely must be to increase the flame diffusion.

The Wallsend-Howden Sprayer (Fig. 1) is a good example of the modern type.

Mechanical Sprayers. These are of two types: (1) those in which the oil stream is disintegrated by forcing under pressure through suitable small orifices, (2) those in which some mechanical baffle or rotating part breaks up the oil stream. For boiler practice only the former calls for description.

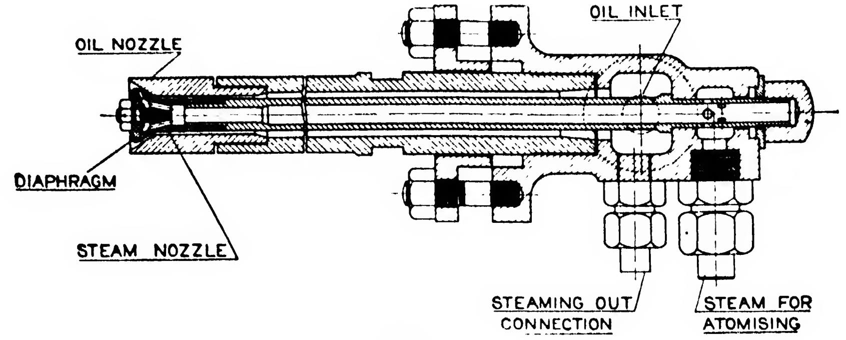


FIG. 1.

(*Reproduced by permission of Messrs. E. Arnold & Co. from 'Fuel' by J. S. S. Brame.*)

For steam-raising purposes, pressure sprayers have largely replaced steam-operated sprayers for shore use and entirely for marine purposes. Their advantages lie in their efficiency, in the use of pumps the steam from which can be returned to the boiler feed, and in their general compactness.

The principle on which all these pressure sprayers are constructed is in forcing the oil at sufficient velocity through orifices so arranged that the oil finally escapes through a single orifice with a powerful swirl, which determines its breaking up into a fine mist.

The viscosity of the oil at the temperature of its emergence from the jet plays an important part in determining the degree of subdivision, and for this reason the oil is always heated. Once the plant is operating there is no difficult in this, but for starting up it is generally necessary to provide some auxiliary heaters. One form of sprayer for marine purposes which enables a start to be made with cold oil is that made by J. Samuel White & Co. (Cowes) (Fig. 2). A small hand or electrically driven pump provides the pressure, and except for oils of viscosity higher than 900 sec. (Redwood I) at or about 60° F. no heating is required. A small auxiliary heater is provided for more viscous oils. The central spindle *D* is coned at the end and carries outside this a projection, the position of which in relation to the orifice can be altered by the hand unit at the other end. For 'cold' spraying it is kept just outside the orifice, acting as a mechanical baffle to the oil stream passing tangentially between the orifice plate *N* and the slot plate *C*. After the plant has heated up, the spindle *D* is drawn back and the sprayer acts in the usual manner. The 'hot' type sprayer has no central spindle.

The Wallsend-Howden sprayer (Fig. 3) has been installed in many of the largest liners. The oil is forced through holes which are drilled nearly tangentially through the diaphragm *D*, causing the oil to swirl rapidly in the inner chamber, and emerge through the nozzle in the plate *C* as a cone of fine spray.

The Clyde sprayer (Fig. 4) is claimed to give satisfactory 'atomization' at pressures from 25 lb. per sq. in. and upwards. Four holes are drilled through the diaphragm *B* at an inclination to the centre axis of the burner, the oil taking up a rotary motion in the conical chamber inside the nozzle piece *C*, which is held in place by the cap nut.

The Urquhart sprayer (Fig. 5) provides for adjustment of the oil output in the burner itself, without alteration of the pressure from the pumps, this being an advantage claimed for it. The swirl is imparted to the oil by the three-start spiral thread *A*, cut on the solid spindle *D*, the depth of the threads varying from zero to a maximum along their length. The area of the three oil exit channels so formed is varied by means of the hand-wheel working in the

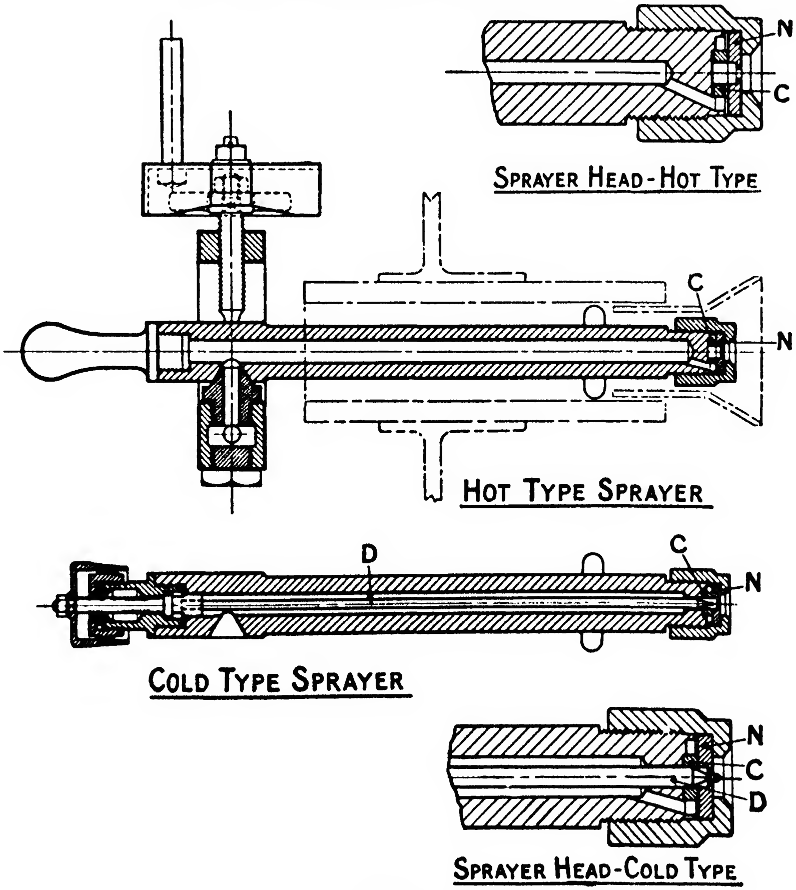


FIG. 2.

(*Reproduced by permission of Messrs. E. Arnold & Co. from 'Fuel' by J. S. S. Brame.*)

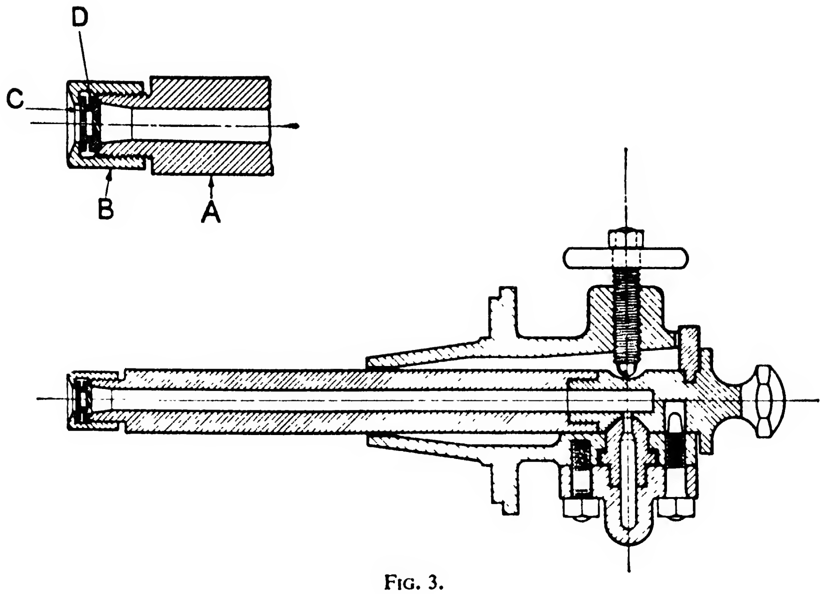


FIG. 3.

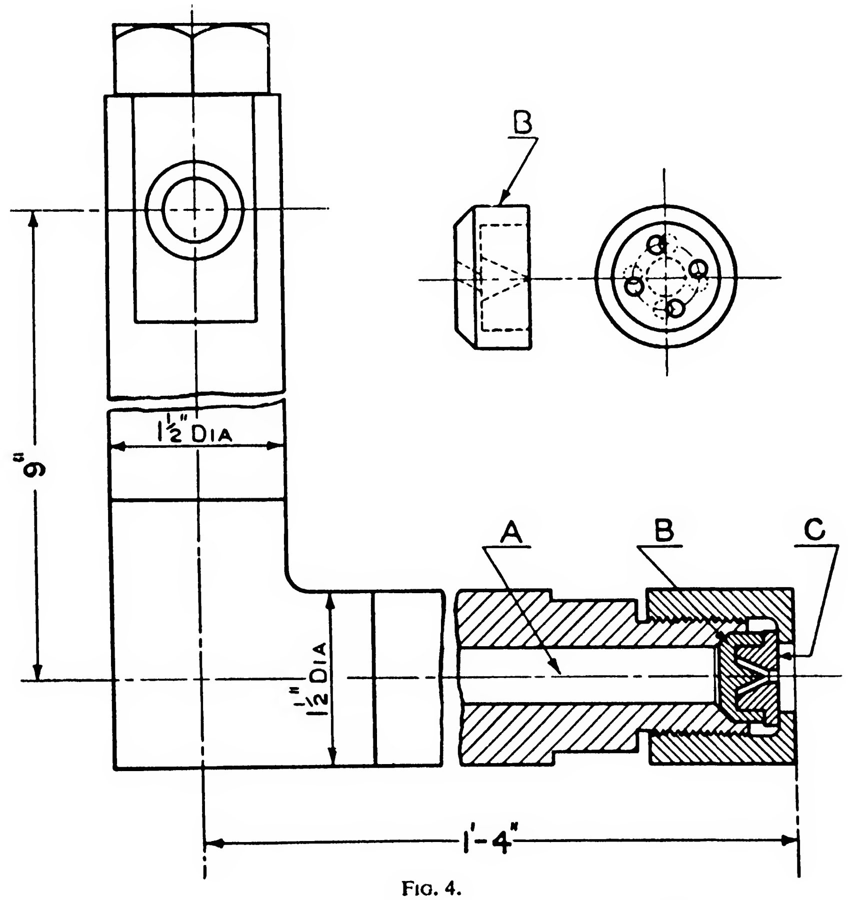


FIG. 4.

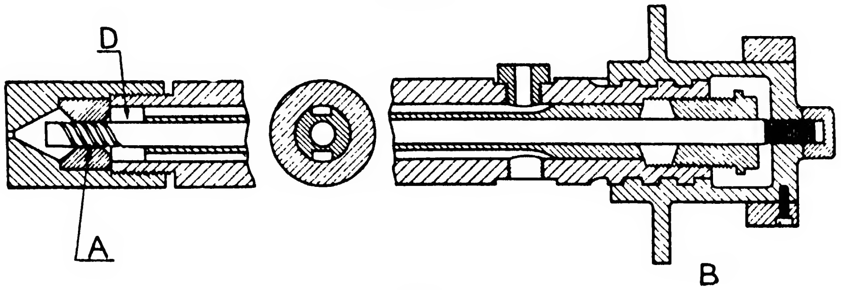


FIG. 5.

(Figs. 3–5 reproduced by permission of Messrs. E. Arnold & Co. from 'Fuel' by J. S. S. Brame.)

substantial square thread shown. Another feature of this sprayer is the oil channel which is really double, as shown in the cross-section, so that even when the oil exit is closed, hot oil can be maintained in circulation right up to the nozzle.

Oil Pump, Heaters, and Strainers. For the pressure-spraying systems the foregoing are necessary adjuncts. The pumps will give pressures ranging usually from 50 to 150 lb. per sq. in., and an air vessel on the pressure side serves to equalize the pressures. Strainers are always duplicated, so that the gauze on one side may be removed for cleaning without interruption of the flow. On the suction side fairly coarse gauze is used; after passing through the heaters the oil passes the second strainers, which are either of very fine mesh or consist of one of the more modern multi-plate filters, with ready means of clearing off the deposited sediment.

Pressure gauges on either side of the strainers indicate when the strainers are becoming dirty.

Before lighting up the sprayers it is necessary to bring the oil up to a sufficiently high temperature for satisfactory spraying, so a ring circuit is arranged round which the oil is circulated until the desired temperature is attained for the sprayer to be put in operation.

The oil must not be too highly heated, or irregular operation of the sprayers results, with probably 'spluttering'. In general it should seldom be heated higher than its flash-point. Care must be taken that it does not become overheated when the oil circulation is reduced.

Special provision must be made for starting up; thus steam must be raised for pumps, unless these are electrically driven. Installations, therefore, will include in most cases hand-operated oil pumps, special paraffin burners of the primus type for a small boiler, and an independent small oil-heating coil.

Preliminary Treatment of Oil. Where the fuel oil will be reduced to a low temperature during storage, tanks, &c., usually have to be equipped with lengths of steam piping for heating, viscous oil being too thick otherwise for pumping. In particular this is the case with oil carried in the double bottoms of ships. One large firm recommends providing 1·5 sq. ft. of heating surface per ton of oil for double bottoms, and 0·65 sq. ft. for deep tanks. Another, 0·75 sq. ft. per ton for tanks with a capacity of 100–500 tons, and 0·5 sq. ft. for tanks of 500–1,000 tons capacity.

Some asphaltic fuel oils increase in viscosity very considerably when maintained at low temperature for long periods.

Where tanks may have had water in previous to the oil fuel (e.g. double bottoms) or there is any danger of the oil becoming contaminated with water, it is always advisable to provide special 'settling' tanks, holding several hours supply and provided with steam-heating coils. These coils should have a surface area of about 1 sq. ft. per cu. ft. tank volume. The oil suction or delivery pipe from the settling tanks is naturally arranged to be well above the level to which any water may rise, and special drain cocks are provided for the water to be drawn off. With steam spraying the oil is fed by gravity so that settling tanks are arranged at a sufficient height. The tanks should be of a deep pattern and be provided with catch trays beneath for any oil leakage.

From viscous oils, which are generally of high specific gravity, water has little chance of settling at ordinary temperatures. By heating, two changes occur which lead to more ready separation of the water; the viscosity of the oil is reduced and, owing to its having a greater coefficient of expansion than water, the effect is so to increase the difference in specific gravity that separation more readily occurs. The relative coefficients of expansion are:

	Oil	*Water*
Per °F. . .	0·00039	0·000264
,, °C. . .	0·00070	0·000476

The capacity of tanks must obviously be such that sufficient time is allowed for separation, and a minimum is about 5 hours' supply, though obviously where space permits larger tanks which will allow of much longer time are advisable.

The presence of finely disseminated globules of water in the oil has little effect in practice, but if the water is in sufficiently coarse state temporarily to interrupt the jet of burning oil, it may give rise to serious trouble, even to a 'blow out' from the furnace.

Air Supply. For smokeless combustion it is highly important that thorough intermingling of the air with the oil mist is ensured. If this is satisfactory, nothing like so much excess air is required per lb. of oil as per lb. of coal, with consequent better evaporative efficiency. Theoretically about 13·8 lb. of air, or 180 cu. ft. (at 60° F.), are required per lb. of oil. Special provision is made on the boiler front for introducing the air, whether with natural or forced draught. Some steam sprayers are designed to act as injectors and draw in a supply of primary air, supplemented by further air admitted round the cone of spray. With pressure burners it is usual to have a proportion of the air admitted round the sprayer and the main supply through a concentric chamber which is provided with a closing device to regulate the amount, and vanes to give a good rotary swirl to the air, this being usually in the opposite direction of rotation to the oil spray.

Special Regulations for Oil Fuel at Sea. Rules for the construction of storage and settling tanks have been adopted by Lloyd's Register, the British Corporation, and the Bureau Veritas. In 1920 the Board of Trade appointed a committee to advise on the conditions and precautions to be observed where oil fuel was burnt in passenger steamships. Points of outstanding importance may be briefly summarized; they will serve as a good guide to those points which, in other cases, should receive consideration.

The construction of storage and settling tanks should meet the requirements of the above-mentioned Registering Authorities. Each oil-fuel tank or bunker must be fitted with an air pipe the discharge end of which is to be led to the open air in a situation where no danger will be incurred from the issuing oil vapour when the tank or bunker is being filled, and each must be furnished with a wire gauze diaphragm which can readily be removed for cleansing or renewal.

Suitable means are to be provided for ascertaining the oil level in each tank, either by sounding pipes or by approved indicating apparatus. Provision must be made to prevent danger from any overflow when filling tanks or bunkers.

Where there is a possibility of oil leakage from storage tanks, settling tanks, pumps, heaters, &c., suitable gutters or coffer dams are to be arranged, and the drainage from the same led to sumps or wells.

Save-alls are to be provided under the pumps, heaters, and strainers where necessary to catch oil that may be spilled when any cover or door is removed, and likewise at the furnace mouths to intercept oil escaping from the burners.

Settling tanks must be tested to a pressure of 15 lb. per sq. in.

The pumps for the oil-fuel burning system must be entirely separate from the feed, bilge, and ballast pumps and connexions. There must be not fewer than two units (a unit comprising pressure pump, filters, and heater).

All oil-fuel suction pipes from storage or settling tanks placed above the double bottom are to be furnished with cocks or valves secured to the tanks and so geared that they may be shut off from the deck above or from a compartment other than the one in which they are situated, as well as from the latter compartment.

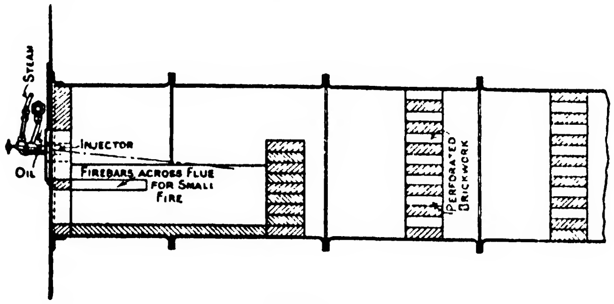


Fig. 6.

(*Reproduced by permission of Messrs. E. Arnold & Co. from 'Fuel' by J. S. S. Brame.*)

For all oil-fuel pressure pumps in each compartment means are to be provided for shutting off the steam supply to the oil-fuel pressure pumps from a position outside the compartment in which the pumps are situated.

The conditions requisite for the production of the short hot type of flame suitable for steam raising, as stated by the United States Navy Fuel Board, were : (1) the fuel should be a pure carbon-hydrogen oil; (2) there should be initial heating of the air; (3) intimate diffusion of the fuel and air; (4) a large surface of fuel exposed to the impact of the air.

In water-tube boilers there is ample combustion space, lined with fire-brick, and beyond the usual baffles to determine the path followed by the hot gases, no further fire-brick is required in the furnace proper. It is usual, however, to have a suitable fire-brick ring around the throat of the furnace: temperatures are here very high and the brickwork protects the metal plates. It is important that the opening towards the furnace shall be well clear of the cone of oil spray.

With boilers having a narrow restricted furnace, as in the case of Lancashire boilers, it is usually necessary to arrange for a fire-brick arch and/or chequers. A typical arrangement for use with a Holden steam sprayer is shown in Fig. 6. Properly arranged, such brickwork helps in the final stages of combustion, maintaining a high temperature where some checking, with the formation of smoke, is otherwise very liable to occur. As the temperature of oil flames is very high it is essential that only the highest grade of brick be used.

Precautions against Fire

The most important and very obvious consideration is the avoidance of any accumulations of oil and, therefore, of any leakage from joints, valves, pumps, &c. On board ship any collection of oil in bilges is to be particularly avoided. Means for dealing with small fires include the provision of sand, or, better still, a mixture of sawdust and bicarbonate of soda—the latter, under the heat of a fire, evolving carbon-dioxide gas. In addition to the usual hose for dealing with fires, the Committee which dealt with the regulations for burning fuel oil in passenger ships, recommended that one of these hoses should be provided with a nozzle to give a fine water spray. Further, that provision for admitting steam into the lower parts of the boiler-room should be provided, with the control of the discharge outside the boiler-room.

In many installations, especially marine, one of the well-known foam systems of extinguishing oil fires is provided, this likewise being put into action from outside the boiler-room.

REFERENCE

1. Bailey, A. F. *J. Roy. Soc. Arts*, **69**, 563,231 (1921).

COAL-IN-OIL SUSPENSIONS

By A. B. MANNING, D.I.C., M.Sc., Ph.D.

Fuel Research Station, Department of Scientific and Industrial Research

Introduction

WHEN referred to a thermal basis, coal is, in general, much cheaper than fuel oil, but a liquid fuel permits a better utilization of the available storage space and can be more readily transported. From time to time attempts have been made to combine these advantages by preparing a mobile suspension of finely pulverized coal in oil for use as a fuel. To fulfil its purpose such a composite fuel should be stable, i.e. no appreciable separation of the coal should occur during the necessary period of storage; it should, moreover, be capable of utilization without difficulty in the type of furnace and auxiliary equipment normally used with liquid fuels. In addition to the advantages arising from mobility the coal-oil suspensions compare favourably with coal and/or oil in other respects. They are, for example, the most compact fuels known and permit the storage of more heat units per cu. ft. of available space than oil alone; thus a 40 : 60 mixture of bituminous coal (calorific value 14,500 B.Th.U. per lb., density 1·35) and fuel oil (calorific value 19,000 B.Th.U. per lb., density 0·9) has a heat value equivalent to nearly 11·2 therms per cu. ft. as compared with 10·7 for the oil alone, or 7·2 (approx.) for the coal. The coal-oil suspensions contain, of course, amounts of ash and moisture intermediate between those of the separate components, in this respect comparing favourably with the coal, but unfavourably with the oil alone. They are immune from spontaneous heating. Their density is greater than unity (e.g. 1·04 in the example quoted above) so that they may be fire-proofed by a 'water seal' of an inch or more in depth; hence also they will sink if they fall blazing on to the surface of water, i.e. they are self-quenching in such circumstances. The possibility of using a water seal has also the advantage of diminishing losses by evaporation.

The coal-oil suspensions have sometimes been referred to as 'colloidal fuels', but the name is frequently a misnomer. Although attempts have been made to form colloidal suspensions of coal in oil, the technical application of such processes would appear to be economically difficult, if not impossible. The diameter of the particles of coal in a practicable coal-oil fuel may range from approximately 5 to 65 μ or even higher, whereas the upper limit of diameter of colloidal particles is approximately $0{\cdot}1\,\mu\,(\mu = 0{\cdot}001$ mm.).

No extended use has yet been made of coal-oil suspensions as fuels, and the only experimental evidence available on which to base a judgement of the value of such fuels consists of a limited number of sporadic tests, the reported results of which, moreover, cannot all be regarded as equally authoritative. The more important of these tests and the results obtained are briefly reviewed below.

Large-scale Tests

During the War, when the question of the conservation of fuel oil had become urgent, the development of a coal-oil fuel was stimulated by the 'Submarine Defense Association', a body formed in 1917 by a number of American shipping, insurance, and oil companies. This organization, under the chairmanship of Lindon W. Bates, initiated work which led to the development of a stable coal-oil suspension [3]. Trials using this suspension as a fuel were carried out under service conditions in the U.S. Scout *Gem* from April to July 1918, with results stated to have been satisfactory in every respect. Successful land tests were also made with a similar fuel. The fuel used in the first trial in the U.S.S. *Gem* consisted of Pocahontas coal 31·2%, Texas fuel oil 67·8%, and 'fixateur' (see below) 1·0%. The coal had a calorific value of 13,974 B.Th.U. per lb. and a sp. gr. of 1·39 at 25° C. It was pulverized so that 99·7% passed a 100-mesh screen, 98% passed a 200-mesh screen, and 85% passed a 300-mesh screen. It is stated, however, that whereas such a degree of fineness is advantageous for combustion efficiency and fluidity as well as stability, it is not strictly essential. The fuel oil had a calorific value of 18,699 B.Th.U. per lb. and a sp. gr. of 0·92 at 25° C. Its viscosity at 20° C. was 18·1° Engler, and at 30° C. 9·3° Engler. The calorific value of the composite fuel was 17,100 B.Th.U. per lb. and its sp. gr. was 1·035 at 25° C.; its viscosity was 170° Engler at 70° F. The mixture of the coal and oil was effected without intensive grinding. The fuel was stable for more than 4 months. Large-scale work on this fuel seems to have ceased after the War, but Bates took out a number of patents which disclosed the methods of stabilizing the coal-oil mixtures, kept secret during hostilities [3]. The most important of these consisted in adding to the mixture a small quantity of a lime-rosin grease ('fixateur') which was prepared by mixing slaked lime with a hydrocarbon oil, adding rosin to the heated mixture, and saponifying the product. Another method consisted in adding about 10% of a coal-tar oil to the petroleum fuel oil used.

In 1922 J. G. Robinson carried out a series of experiments on the firing of Great Central Railway locomotives with pulverized fuel and with mixtures of pulverized fuel and oil [9]. The latter were apparently used soon after they were made up, no attempt being made to stabilize them by the addition of suitable agents or other special treatment. The following data relate to one of these trials:

The fuel consisted of	Elsecar coal dust .	60%
	Fuel oil . .	40%
Method of preparation		mixed by air-blowing
Moisture		1·15%
Ash		4·40%
Calorific value		16,427 B.Th.U. per lb.
Total fuel consumed		2,965 lb.
Overall efficiency		72%

Other fuels tested were made up with coal-tar oils. They all, apparently, behaved satisfactorily in practice. The following remarks may be quoted from the description of these trials: 'Although, under normal circumstances, locomotives equipped in the manner we have described are not a commercial proposition in this country, owing to the presence of moderately priced, good quality coal, yet they undoubtedly are, and in fact have proved themselves to be, of great value in the event of coal strikes or other emergencies. On the other hand, there is almost illimitable scope for their use in India, South America and the Colonies, where high-grade fuel is difficult to procure as compared with oil and coal of inferior quality.'

After a period of quiescence interest was again greatly stimulated in coal-oil fuels, especially for marine purposes, by the voyage of the S.S. *Scythia* of the Cunard Company in the round trip between Liverpool and New York, which terminated in the first week of July 1932, and in which one boiler, out of a total of twelve, normally fired with oil, was fired with a coal-oil suspension [7]. The fuel had been developed as the result of experiments carried out in the Cunard Company's own laboratory; large-scale tests confirmed the laboratory results, and, in order to make the above-mentioned trial, about 150 tons of the fuel were manufactured. No difficulty was experienced in storing, handling, or burning the fuel, which was dealt with through the ordinary oil-fuel equipment. The jets of the burners had to be cleaned somewhat more frequently than when oil alone was burned. It was not possible to measure separately the amount of steam generated by the one boiler, but from such observations as could be made there was good cause to believe that the steam output and the efficiency of the boiler using the coal-oil fuel were identical with those of similar boilers using oil fuel; this was subsequently confirmed by shore trials. The fuel contained 40% of powdered bituminous coal, ground to pass a 200-mesh I.M.M. sieve; the coal was dispersed in the oil, without further grinding, by passing the mixture through a homogenizer.

The fuel remaining over from the experiment was found to be perfectly stable and unchanged 9 months after it had been prepared. The essential details of the discovery were disclosed in a patent specification published in August 1933 [7]. According to this the fuel is made by mixing finely pulverized coal with a cracked fuel oil having a 'fixed carbon' content of not less than 5%. The 'fixed carbon' content of the oil is determined by heating 1 g. in a silica crucible to about 900° C., under specified conditions, and weighing the residue.

In Germany tests were carried out in 1932 with a fuel ('Fliesskohle') consisting of a mixture of 55% of powdered coal and 45% of tar oil, prepared by the Maschinenbau A.-G. Balcke [26]. A boiler of the single fire-tube (Cornish) type, fitted for oil firing, was used. The fuel was stable and sufficiently mobile, its transfer from barrels to the pressure vessel and thence to the burners offering no difficulty. The fuel ignited readily and burned, with suitable regulation of the firing, especially with regard to the ratio of primary to secondary air and to the pressure in the atomizer, with a clear, luminous, white flame, practically smoke-free. In two tests thermal efficiencies of 70·5 and 74·7% were obtained, and it was estimated that considerably higher efficiencies, e.g. 81%, could be obtained in continuous operation. Data concerning the method of preparation and the stabilizer used are not available. The tar oil used was an anthracene oil having a distillation range of approximately 270–330° C.; the composition of the coal used and of the 'Fliesskohle' are given below:

	Coal	*'Fliesskohle'*
Moisture %	. .	1·80
Ash %	6·39	3·48
Carbon %	82·75	84·17
Hydrogen %	4·60	5·55
Sulphur %	1·03	0·64
Oxygen and nitrogen %	5·23	4·36
Calorific value (gross)	8,010–8,060	(estimated)
	8,525 kg.-cal. per kg.	
Volatile matter %	22·37	57·42

88% of the coal passed a sieve having 10,000 meshes per sq. cm. The Maschinenbau A.-G. Balcke claims to have produced similar stable fuels using mineral oils instead of coal-tar oils.

S. L. Wyndham has recently developed a process for preparing a coal-oil fuel, the stability, mobility, and combustion properties of which are due to the fine division of the coal particles effected by grinding a mixture of oil with the initially coarsely ground coal in a series of specially designed mills [31]. The most suitable proportions are 50% of coal and 50% of oil. The fuel is said to be stable for a minimum period of 4 months at the normal temperature. A demonstration was made of the process on 23 January 1935, in which the fuel was burned under a cross-tube vertical boiler 6 ft. in diameter and 12 ft. high. A specially designed burner of the air-atomizing type was used; the fuel was preheated to about 200° F.; the pressure in the fuel was 15–20 lb. per sq. in. and the air pressure 2 lb. per sq. in. A perfectly clear flame was obtained and no traces of smoke or grit were observed at the stack. Figures for the boiler efficiency have not yet been published. The particular fuel used in the demonstration consisted of 50% of washed duff supplied by the Ocean Coal Co. (calorific value 14,360 B.Th.U. per lb.) and 50% of an Anglo-Iranian fuel oil (calorific value 19,373 B.Th.U. per lb.).

Stability of Coal-oil Suspensions

A suspension of pulverized coal, of sp. gr. say 1·3, in fuel oil, of sp. gr. say 0·9, will in general be unstable, and the coal will settle out at a rate dependent on (*a*) the size of the particles, (*b*) the viscosity of the oil, and (*c*) the concentration of the mixture. In order that the suspension shall conform with the requirements of a technical fuel it should possess a certain degree of stability; thus, for marine purposes no appreciable settling should occur on storage at the atmospheric temperature in 5–6 months, or at higher temperatures, e.g. 50–100° C., in a few hours. The methods used for conferring this stability on the composite fuel may be classified as follows: (*a*) mechanical reduction of particle size of the coal, (*b*) conferring a 'gel' structure on the oil by incorporating a suitable agent therein, (*c*) use of a 'peptizing' agent, (*d*) choice of certain types of oil which give stable coal-oil suspensions without the necessity of adding a stabilizing agent or other treatment.

The production of a stable coal-oil fuel by grinding the coal to colloidal dimensions was suggested by Plauson in 1913 [19] and again in 1920 [20]. He ground mixtures of coal and oil in a high-speed colloid mill, in some cases adding also a protective colloid, e.g. soap, casein, gelatin, rubber, &c. He claimed that such a fuel prepared from a coal containing not more than 10% of ash would be suitable for use in an engine of the Diesel type. The process, however, was a costly one and does not appear to have had any industrial application. The stability of the fuel prepared by Wyndham (see above) is attributed to the particular type of intensive grinding to which it is subjected; it is claimed that a proportion of the coal is reduced to a colloidal or semi-colloidal condition. The greater part of the coal, however, appears to be of a size well outside that of the colloidal range. Wyndham claims also that the cost of grinding in his process is not excessive.

The economic limit of the size to which the coal can be reduced without incurring excessive grinding costs appears to be of the order of that used in normal pulverized fuel firing practice, i.e. 80–90% through a 200-mesh I.M.M. sieve, or perhaps slightly finer, corresponding to a range of particle size from approximately 0·0025 in. (64μ) in diameter downwards. A suspension in oil of coal of this size can be rendered stable by converting the oil into a dilute gel, as was realized by Sheppard [27]. A dilute gel has the property of flowing like a liquid under normal circumstances, but of behaving like an elastic solid under very small distorting forces, such as are called into play in supporting small particles of coal. If the 'yield value' of the gel is greater than the maximum stress due to the weight of a suspended particle, then the suspension is stable. Such a structure can be conferred on the oil by dispersing a small amount of a suitable agent, e.g. 0·2–1·0% of sodium stearate (soap), therein. The method of dispersion may be important; thus if sodium stearate is used it is necessary, in order to produce the full effect, to dissolve this in the oil at about 200° C. and then allow to cool. A suspension of 40% of pulverized coal, 85% of which passed a 200-mesh I.M.M. sieve, in an Iranian fuel oil in which 0·5% of sodium stearate had been dispersed, showed no appreciable separation of coal after standing at the atmospheric temperature for 5 months; after 10 hours at 100° C., however, the gel structure had disappeared and the coal began to separate out. A similar suspension in the original untreated oil showed signs of separation after 20 days at the atmospheric temperature [22]. It is probable that many of the other stabilizing agents, 'fixateurs', or so-called 'protective colloids', the use of which has been suggested, act in a similar manner by conferring a gel structure on the oil. The 'fixateur' preferred by Bates (see above) would probably have such an action.

It is known that certain oils, in particular high-boiling tar oils, have the property of dispersing bituminous coals more or less completely when the powdered coal and oil are heated together, the coal passing into colloidal solution in the oil [13, 8, 18]; the process is known as 'peptization' of the coal. It has been found that the addition of tar oils to suspensions of finely divided coal in petroleum fuel oils has sometimes the effect of stabilizing the mixture. The effect is due probably to a partial peptization of the coal, such process conferring some type of structure on the oil phase, possibly converting it into a dilute gel, which thus is enabled to support the remaining unpeptized coal.

It is possible to confer sufficient structure on some oils for them to be capable of forming stable suspensions of pulverized coal by the simple process of blowing air through the heated oil, the stabilizing agent being an oxidation product of the oil itself [1, 10, 14].

Particular interest attaches to the Cunard Company's discovery that some fuel oils, in particular certain oils produced in cracking processes and normally available on the market as fuel oils, form stable suspensions of pulverized coal (of the economic size mentioned above) without the necessity of adding a stabilizer or of any other pretreatment of the oil. This discovery has been confirmed by experiments carried out at the Fuel Research Station [23]. Not all oils, however, having a 'fixed carbon' content greater than 5% give stable suspensions. The oils in question, or at least some of them, do not appear to possess a gel structure in that they exhibit no measurable rigidity, nor do they peptize the coal; they do, however, possess a type of structure which resembles a gel structure in being characterized by the possession of anomalous viscous properties, i.e. they possess a coefficient of viscosity which increases with diminishing rate of shear (velocity gradient). It has been suggested that this may account for the observed stability of the coal suspensions in these oils [14].

A convenient method of examining the stability of coal-in-oil suspensions in the laboratory has been devised by R. A. A. Taylor [14]; it is based on observing the variation in the period of oscillation of a tube filled with the suspension, which is mounted in a holder in such a manner that the system functions as a compound pendulum.

Brief mention may be made of the influence of concentration of a suspension on its rate of settling. The rate of fall of a single particle of coal through an oil of normal viscous properties (a so-called Newtonian liquid) is given approximately by Stokes' law. When dealing, however, with the rate of fall of a large number of particles distributed throughout the liquid Stokes' law is no longer applicable. The mathematical analysis of this problem is difficult, but the order of magnitude of the effect is shown by the following experimental results on the rate of fall of a suspension of finely divided coal (through a 200- and on a 240-mesh B.S.I. screen) in a heavy paraffin oil (viscosity 0·75 poises).

Concn. of coal in the suspension	*Rate of settling cm. per sec.*
Single particle	0·00167
9%	0·00079
23%	0·00024
40%	0·00003

It is of interest to note that the coal in a 50:50 coal-oil suspension is already more closely packed, before any settling begins, than it is normally when in the form of dry pulverized fuel.

The Combustion of Coal-oil Suspensions

The results of the full-scale tests that have been carried out with coal-oil fuels show that these fuels can be burned quite satisfactorily in suitable types of equipment. Observation of the flame produced by combustion of this fuel indicates that the two constituents burn more or less independently, the oil first and then the coal. It is necessary, therefore, as with pulverized fuel firing, to provide sufficient space to permit complete combustion of the slower burning solid particles before the flame impinges on the tubes of the boiler, otherwise the latter will rapidly become covered with a deposit of incompletely burned material. Moreover, again as with pulverized fuel firing, it is desirable that combustion should be so controlled that slagging of the ash is avoided; provision must be made, of course, for the removal of any ash that is deposited. It has been stated that owing to the presence of radiant particles in the flame, and to a decrease in the water-vapour content of the flue gases, coal-oil fuel is about 2% more efficient as a steam producer than oil [33]. Combustion is improved if a small amount, e.g. 3%, of water is added to the fuel, preferably just before it reaches the burner. The S.S. *Scythia* was equipped with Scotch marine boilers, a type which appears to be eminently suitable for firing with coal-oil fuels. No modification was found to be necessary in the normal oil-fuel equipment. The ash was almost impalpable and its disposal offered no difficulty. In preparing the fuel for this test the coal was ground to pass completely through a 200-mesh I.M.M. screen, i.e. rather finer than was necessary to ensure stability in the fuel, in order to avoid any choking of the jets of the oil burners; probably a somewhat coarser coal could be used with specially designed jets. The German tests show that, as was perhaps to be expected, coal-oil fuels can be burned satisfactorily in the Cornish type of boiler. Attention may be directed to the fact that a tar oil was used in the preparation of the fuel used in these tests, and it is noteworthy that such a mixture can be burned apparently with no greater difficulty than suspensions of coal in petroleum fuel oils. Coal-oil fuels would probably be quite unsuitable for firing the 'three-drum' boiler of the type used extensively in the Navy; the combustion space is too limited, and ash and incompletely burned fuel would tend to collect in the somewhat narrow apertures between the water-tubes.

Economic Considerations

It is evident that in considering the economics of the use of coal-tar fuels certain of the factors involved will vary considerably with locality and with other special circumstances that cannot be taken into account in a general discussion of the question. It can readily be shown (cf. [26]) that if P_c is the cost of the coal and P_o the cost of the oil, in shillings per ton, including freight to the grinding and mixing plant, if M_g is the cost of drying and grinding the coal, in shillings per ton, if M_m is the cost of mixing, in shillings per ton of coal-oil fuel, including freight from the grinding and mixing plant to the place of utilization, if H_c is the calorific value of the coal and H_o that of the oil, in B.Th.U. per lb., and if k is the proportion by weight of coal in the mixture, then the cost of the coal-oil fuel is

$$k(P_c+M_g)+(1-k)P_o+M_m \quad \text{shillings per ton, or}$$

$$\frac{\{k(P_c+M_g)+(1-k)P_o+M_m\}12}{\{kH_c+(1-k)H_o\}\,0{\cdot}0224} \quad \text{pence per therm.}$$

Applying this, for example, to a 40 : 60 coal-oil suspension and using the following estimates

P_c 15*s*. per ton, H_c 14,000 B.Th.U. per lb.
P_o 40*s*. per ton, H_o 19,000 B.Th.U. per lb.

M_g 2*s*. per ton (including cost of power, labour, and maintenance, depreciation and interest on capital. Cf. [15].

M_m 7*d*. per ton

we have

Cost of composite fuel, 31*s*. 4½*d*. per ton
or 0·989*d*. per therm

as compared with

Cost of oil, 40*s*. per ton
or 1·127*d*. per therm.

The cost of a plant capable of preparing 500 tons of coal-oil fuel per day has been estimated as approximately £9,000. Such a plant would already consist of more than one unit, so that the cost of a plant of larger capacity would be proportional to the capacity.

In the above calculation it has been assumed either that no stabilizing agent was necessary, which, as we have seen, is true for certain oils, or that if such an agent is used its cost has been included in that of the oil. It would appear that at the present time (May 1935) the cost of fuel oil is at such a level that the economic advantage of replacing oil by coal-oil suspensions is hardly sufficient to favour adoption of the newer fuels. The position, however, may change in the future, and any tendency towards higher fuel-oil prices will focus more interest on the possibilities of using coal-oil suspensions as fuels. In some localities even now economic conditions exist under which the possibility of using coal-oil fuels merits careful consideration.

REFERENCES

Of the references given below nearly all those not already referred to in the text are to patents claiming methods of preparing stable coal-oil suspensions which have not as yet led to any practical developments of importance.

1. Amer. Coalinoil Corp. B.P. 292,673 (1927); B.P. 332,343 (1929.)
2. Armstrong, J. J. V. B.P. 155,212 (1920).
3. Bates, Lindon W. *Colloidal Fuel* (pamphlet privately printed in 1918), 184 pp.; *Colloidal Fuel* (pamphlet printed by the Submarine Defense Association, 1918), 29 pp.; *J.S.C.I.* **39**, 395 R, 413 R (1920); *Chem. Age*, **3**, 558-9 (1920); B.P. 149,306 (1919); B.P. 165,418-23 and 165,425 (1919).
4. Benthin, G. *Proc. World Petr. Cong.* **2**, 813-15 (1933); *Angew. Chem.* **46**, 742-4 (1933).
5. Calvert, G. B.P. 14,656 (1912).
6. —— B.P. 163,797 (1920).
7. Cunard Steamship Co. *Times*, 13 June and 6 July 1932; *Colliery Guard.* **144**, 1179 (1932); **146**, 639 (1933). Cunard Steamship Co., Adam, R.A., Holmes, F. C. V., and Perrins, A. W., B.P. 396,432 (1932).
8. Gillet, A. *Proc. Third Internat. Conf. Bituminous Coal*, **2**, 1 (1931); Gillet, A., and Pirlot, A., *Bull. Soc. Chim. Belg.* **41**, 511 (1932).
9. Great Central Railway. *Modern Transport*, **7**, no. 168, 3 (1922).
10. Greenstreet, C. J. B.P. 179,567 (1920); U.S.P. 1,431,225 (1922); U.S.P. 1,432,178 (1919).
11. —— B.P. 362,424 (1930).
12. Kern, L. U.S.P. 1,899,811 (1933).
13. Koppers Co. B.P. 268,372 (1927).
14. Manning, A. B. *Proc. World Petr. Cong.* **2**, 811-12 (1933); Manning, A. B., and Taylor, R. A. A. Paper read before the Inst. Chem. Eng., 21 Feb. 1936. *J. Inst. Fuel*, **9**, 303-11 (1936).
15. Memo. No. 9 of the Utilization of Coal Committee, Inst. of Mining Engineers, Feb. 1933. Also Summary of Progress No. 1, June 1933.
16. Nesfield, A. C. B.P. 406,675 (1932).
17. Oda, R., and Wada, S. *J.S.C.I. Japan*, **37**, 294-5 B (1934).
18. Pertierra, J. M. *Anal. Fis. Quim.* **31**, 271-88 (1933).
19. Plauson, H. B.P. 17,729 (1913).
20. Plauson, H. *Chem.-Ztg.*, **44**, 553, 565 (1920).
21. Radiochemisches Forschungsinst. G.m.b.H. B.P. 406,067 (1932); B.P. 417,352 (1933).
22. *Report of the Fuel Research Board* (1933), 115-16.
23. *Report of the Fuel Research Board* (1934), 125-9.
24. Roberts, A. A. B.P. 408,951 (1932); B.P. 433,348 (1934).
25. Rose, H. J., and Hill, W. H. Assrs. to Koppers Co., U.S.P. 1,925,005 (1933).
26. Schultes, W. *Glückauf*, **68**, 1198 (1932); *Proc. World Petr. Cong.* **2**, 816-20 (1933); *Steam Engineer*, **5**, 203 (1933).
27. Sheppard, S. E. *Ind. Eng. Chem.* **13**, 37 (1921).
28. Smith, H. R., and Munsell, H. M. U.S.P. 219,181 (1879). This appears to be the first mention of the proposed use of mixtures of coal and oil as fuel.
29. Spelman, M. U.S.P. 776,365 (1904).
30. Strevens, J. L. B.P. 323,773 (1928).
31. Wyndham, S. L. B.P. 410,883 (1933); *Fuel Econ.* **8**, 280 (1933); *Iron and Coal Trades Rev.* **130**, 178 (1935); *Steam Engineer*, **4**, 248-9 (1935); *Engineering*, **139**, 117 (1935).

Reference may also be made to the following books and general articles or reviews discussing the use of coal-oil fuels or containing references thereto.

32. Brame, J. S. S. *J.S.C.I.* **51**, 855 (1932).
33. Brand, J. C. *Fuel Econ.* **7**, 527-9 (1932).
34. Brownlie, D. *Iron and Coal Trades Rev.* **129**, 671 (1934).
35. Dunn, J. T. *Pulverised and Colloidal Fuel.* Ernest Benn Ltd., 1924.
36. *Engineering*, **137**, leading article (15 June 1934).
37. Harvey, L. C. *Pulverised Fuel, Colloidal Fuel, Fuel Economy, and Smokeless Combustion.* Macdonald & Evans, 1924.
38. Knox, G. *Proc. S. Wales Inst. Eng.* **48**, 359 (1932).
39. Louis, H. *Engineer*, **154**, 66 (1932).
40. Tollemache, H. D. *Colliery Guard.* **146**, 569, 712 (1933).

LUBRICANTS

LUBRICATION—INTRODUCTORY

By D. R. PYE, M.A., Sc.D., F.R.S., F.R.Ae.S., M.I. Mech. E.
Director of Research, Air Ministry

AT every point where surfaces are in contact, and in relative motion, heat is produced by friction. The problem of lubrication is that of reducing the rate of production of that heat to a minimum, and to something less than the rate at which it can be removed. Between some surfaces in motion past one another it is possible to maintain a flow of the lubricant, so that the surfaces are everywhere separated by a continuous film. When this is so the condition is described as one of 'perfect' or 'film' lubrication. The friction force which opposes relative motion of the surfaces then depends chiefly upon the viscosity of the oil film, and could be calculated in terms of the properties of the oil, if the thickness and temperature of the film at every point were known.

When conditions are not such as to maintain an oil film of finite thickness between the surfaces, the state of affairs is one which is described as 'boundary' lubrication. We are then concerned with the forces between the molecules of infinitesimally thin (in the limit monomolecular) adsorbed films on the solid surfaces, and these forces depend not only upon the shape and structure of the lubricant molecules but upon their orientation on the surfaces. Recent electron diffraction methods have exhibited the molecules of a castor-oil film as orientated in a perfectly regular manner to a depth of three layers on a solid surface; and have shown, also, that when graphite is used as a solid lubricant its power of reducing the friction between two surfaces depends entirely upon the ultimate graphite molecules being orientated in a particular manner so that there are slip-planes parallel to the direction of motion. The subject of boundary lubrication will be dealt with more fully in the second half of the present article, but it is appropriate to mention here that when such a state exists the observed friction, while always lower than that between unlubricated surfaces, is far above that when fluid friction prevails. As compared with coefficients of the order of 0·01 with fluid friction, but varying widely according to the conditions, those with boundary friction would be in the range 0·1–0·3.

Film and boundary lubrication have this in common, that they both depend upon the property of lubricants of being able to wet and adhere to the surfaces with which they are in contact. In the case of boundary lubrication the strength of the chemical bond between the molecules of the lubricant and the solid surface is what determines the ability of the surface to maintain an adsorbed layer of lubricant, and so prevent metallic contact and seizure. In film lubrication, some power of adhesion is also essential to ensure the lubricant being drawn in between the surfaces to form the flowing film. Any possibility of slip between the lubricant and the surfaces to be separated would render film lubrication impossible. It should be understood that the condition to which the names 'perfect' and 'film' lubrication properly apply is necessarily associated with a *flow* of the lubricant itself between the lubricated surfaces; and that there is then in the flowing film a hydrostatic pressure which varies steadily from point to point in a manner which can be calculated from the laws of hydrodynamics. Between this and boundary lubrication there is an intermediate state, which has been called 'greasy lubrication', in which the surfaces are separated by a thin film of lubricant, but no actual flow takes place. This condition would normally be transitional, either just after starting, before the state of film lubrication has had time to establish itself, or else leading to a thinner and thinner film, and ultimately to a state of boundary lubrication. Owing, however, to the unevenness of nearly all lubricated surfaces, the points where the boundary condition is approached are constantly changing, and for this reason lubricated motion is able to continue without seizure, provided the load per sq. in. is not too great, even when conditions are not favourable to the establishment of the flowing film.

The existence of fluid pressure in the oil film which varied regularly from point to point, and could reach a maximum value far higher than the mean load on the bearing, was first demonstrated during a series of experiments by Beauchamp Tower [1, 1883, 1885] in which the frictional torque between a journal and its bearing, of 4-in. diameter and 6-in. length, was measured at different speeds and loads; there being an ample supply of oil at the 'on' side of the bearing, at the point from which oil would be drawn in upon the surface of the revolving journal. By means of holes drilled through the bearing, and connected in turn to pressure gauges, the variation of pressure in the oil film was observed from point to point between the 'on' and the 'off' sides, with its maximum on the 'off' side of the centre line. Fig. 1 shows a typical pressure curve taken from Beauchamp Tower's results. Subsequent experiments of the same kind under more closely controlled special conditions have been made by Stanton [13, 1923], Boswell [2, 1932], and others.

The classical experiments of Beauchamp Tower published in 1885, with the mathematical treatment of the problem by Osborne Reynolds [10, 1886] which followed in 1886, laid the foundation of our knowledge of film lubrication. The work of Reynolds, extended by Rayleigh [11, 1918], Martin [8], Harrison [5, 1913], Sommerfeld [12, 1904], and others, led to the formulation of equations between the variation of oil pressure from point to point, and the velocity, which applied to plain and curved surfaces of infinite width in a direction at right angles to the motion. In practice the finite width of a bearing leads to leakage, and a consequent pressure variation at right angles to the motion; and Michell [9, 1905, 1923] was the first to give a complete solution for the flow of a lubricant in three dimensions between plane surfaces. Basing his designs on this theoretical work, Michell invented his well-known form of thrust bearing, which was introduced about the same time, but independently, by Kingsbury in the U.S.A. It is surprising that the work of Reynolds should have waited 20 years for its practical application, since the original paper of 1886 clearly indicates how the low friction associated with film lubrication between plane surfaces might be achieved in practice.

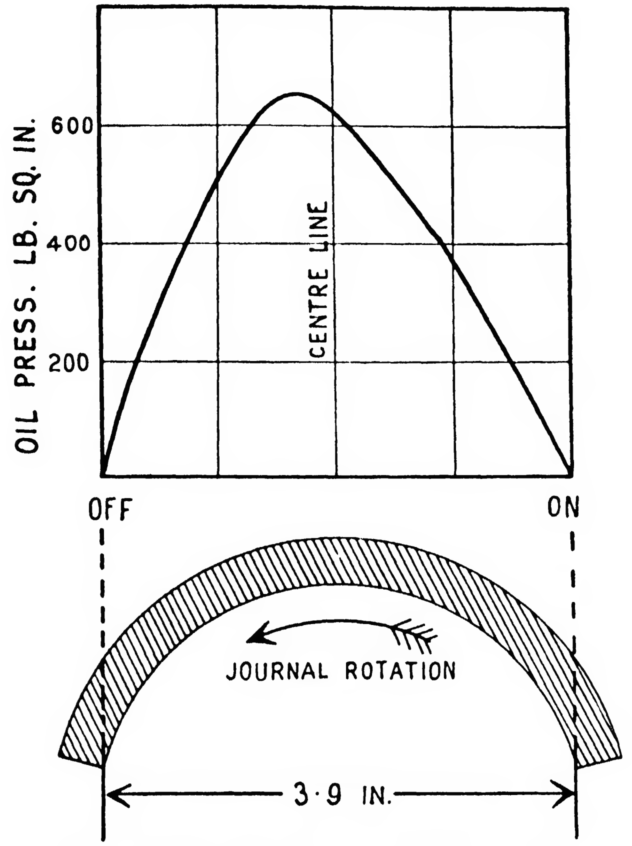


FIG. 1. Nominal mean load on bearing 342 lb. per sq. in.

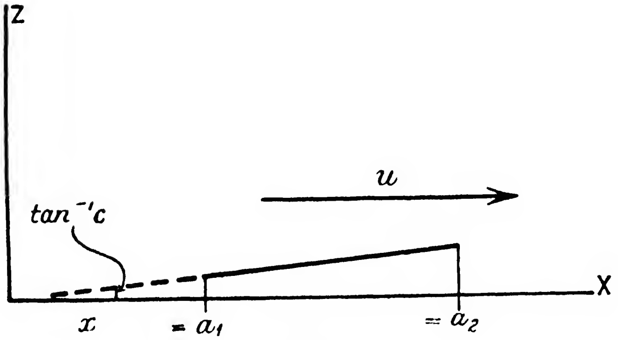


FIG. 2.

Taking the simpler case of a plane bearing of unlimited width (which represents with fair accuracy a bearing from which side leakage is limited by flanges), the essential conditions are represented in Fig. 2, in which the lower surface is supposed to move past the upper, inclined at an angle $\tan^{-1} c$, with velocity u. There will be no changes of oil pressure or velocity in the direction of the y-axis, and the application of the general equations of hydrodynamics leads to the following expression for the pressure between the two plane surfaces at any point at a distance x from the axis of y, along which the two planes would intersect:

$$p = p_0 + \frac{6\mu u}{c^2(a_1+a_2)}\left[\frac{a_1+a_2}{x} - \frac{a_1 a_2}{x^2} - 1\right]. \tag{1}$$

The viscosity of the lubricant, μ, is assumed to be constant, and p_0 is the pressure in the fluid at the positions $x = a_1$ and $x = a_2$. It will be seen, also, that the mean film thickness is assumed to remain constant and equal to $\frac{1}{2}c(a_1+a_2)$.

A particular case in which the assumed conditions apply exactly is that of a conical sleeve drawn along a cylindrical rod, as illustrated in Fig. 3, for considerations of symmetry show that there can be no pressure changes in the direction of the y-axis.

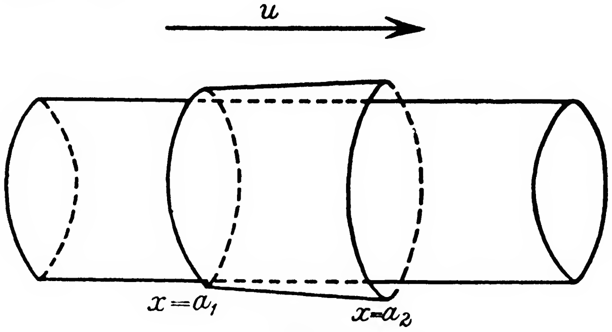


FIG. 3.

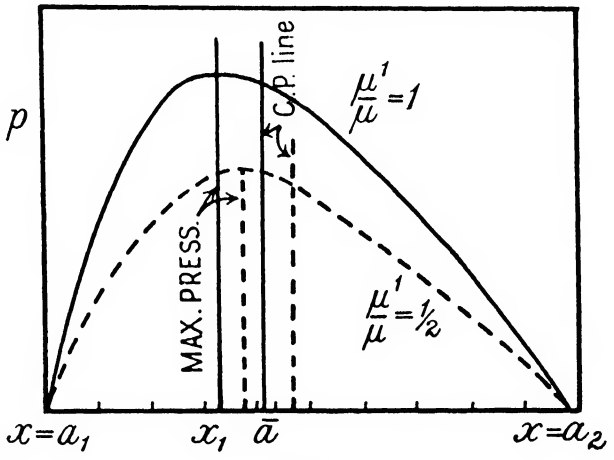


FIG. 4.

The form of the pressure curve given by equation (1) is as shown in Fig. 4, with a maximum value at the point

$$x_1 = \frac{2a_1 a_2}{a_1+a_2}, \tag{2}$$

i.e. on the 'down-stream' side of sleeve, or bearing, centre. The total force tending to separate the bearing surfaces per unit of width is

$$P = \frac{6\mu U}{c^2}\left[\log_e \frac{a_2}{a_1} + \frac{2a_1 - a_2}{a_1+a_2}\right], \tag{3}$$

and the frictional force parallel to x is

$$F = \frac{\mu U}{c}\log_e \frac{a_2}{a_1}, \tag{4}$$

so that the total force needed to draw the sleeve along the rod, in Fig. 3, is

$$2\pi r_1 F = \frac{2\pi r_1 \mu U}{c}\log_e \frac{a_2}{a_1}.$$

For the particular case when $a_2 = 2a_1$ the pressure variation gives a maximum when $x = \frac{4}{3}a_1$, or at $\frac{1}{3}$ of the sleeve-length from the rear end; and the centre of pressure occurs at 0·431 of the length from the same end.

As mentioned above, the theory has assumed that the viscosity remains constant throughout the flowing film. In a heavily loaded bearing carrying, for example, a load of 1,000 lb. per sq. in., it can easily be calculated from considerations of the energy expended in overcoming the viscous friction, and of the heat capacity of the oil film, that, neglecting the heat conducted away by the metal surfaces, there may easily be a rise of temperature of the order of 50° C. between different points in the bearing; and this would, of course, be sufficient to cause wide variations of viscosity.

As an example of the possible effect of a rise of temperature in the film, the dotted curve in Fig. 4 shows how the pressure would vary in the same bearing if the viscosity of the oil were reduced by 50% between the front and rear edges. The important point to notice is the shift of the point of maximum pressure towards the front of the bearing. The centre of pressure has moved up towards the middle point of the bearing, and it is quite possible for the heating of the oil film to be sufficient to shift it up to, or even beyond, this point.

This shift forward of the centre of pressure due to a rise of temperature on the film, has an important practical application in the thrust bearing, for the flowing film can only be maintained if the pads are pivoted, and the external load therefore applied, at the centre of pressure. With a constant viscosity the centre of pressure is eccentric, and maintenance of the film is only possible for motion in one direction. It has been found, moreover, that with oils showing a rapid fall of viscosity with rise of temperature the film can be maintained, with a central pivot, for motion in either direction, by reason of the forward movement of the centre of pressure caused by heating up of the film.

Reverting, now, to the cylindrical bearing, Beauchamp Tower made no attempt to measure the temperature of the oil film, and in his first analysis Reynolds made the assumption that it was the same as that of the oil bath. He soon decided this could not be so, for on the assumption of a constant viscosity and thickness of the oil film the frictional torque would be proportioned to the speed, whereas the experiments showed it to have increased much more slowly. Reynolds concluded, therefore, that the temperature of the oil film must be rising, and its viscosity falling, with increase of speed.

Using an experimental relation between viscosity and temperature for the oil used by Tower, Osborne Reynolds obtained an empirical formula connecting the changes of μ with changes of speed and load, and after taking into account these viscosity changes he obtained complete accord between the experiments and the results of hydrodynamic theory. There followed, therefore, from Reynolds's analysis,

(1) an explanation of the novel phenomena of the pressure variation in Tower's experiments,
(2) a verification of the assumptions of hydrodynamic theory,
(3) an explanation of how the various circumstances in which the experiments were made had affected the results.

These circumstances, which include such factors as the difference between the radii of the journal and bearing, the eccentricity, and the point of nearest approach of the surfaces while running, were not, and could not possibly have been, observed by Tower; and it was left for the mathematical analysis to demonstrate their importance. The points which emerged were:

(1) That for the maintenance of a flowing film it was, in general, necessary for there to be a difference between the radius of the journal and that of the bearing.
(2) That the two cylindrical surfaces would be eccentric to one another while running, by an amount depending on the load, speed, and nature of the lubricant.
(3) That the point of nearest approach of the surfaces was not in the line of action of the load, but would lie on the 'off' side of this line, i.e. towards the point where the oil leaves the bearing after being under pressure between the surfaces.

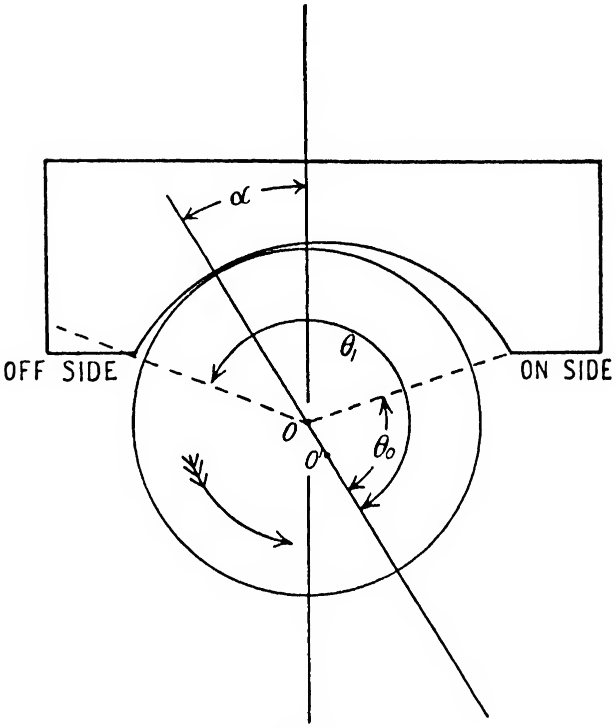


Fig. 5.

In Fig. 5 let O and O' be the centres of the journal and bearing respectively, and let points round the bearing be defined by their angular positions θ from the line OO', in a counter-clockwise direction. OO' passes through the point of nearest approach and makes an angle α with the vertical. Then, if the radii of the journal and bearing are a and $a+\delta$ respectively, and $OO' = c\delta$, the thickness of the film is given by

$$h = \delta(1+c\cos\theta). \tag{5}$$

Assuming the space between the surfaces to be filled with lubricant between the positions θ_0 and θ_1, then Reynolds's analysis showed that the pressure-slope in the film is given by

$$\frac{dp}{d\theta} = \frac{6\mu Uac(\cos\theta - \cos\theta')}{\delta^2(1+c\cos\theta)^2}, \tag{6}$$

in which θ' is the value of θ at the point of maximum pressure, μ is the viscosity of the lubricant, and U the relative velocity of the surfaces. Further, the intensity of the frictional resistance at the surface of the bearing is

$$f = \left[\frac{\mu U}{h} - \frac{h}{2a}\frac{dp}{d\theta}\right]_{z=h}. \tag{7}$$

The bearing is in equilibrium under the load W, acting through O, the fluid pressure and friction, and an externally applied couple M, per unit length. The equations of equilibrium of the bearing are

$$\int_{\theta_0}^{\theta_1} [p\sin(\theta+\alpha)+f\cos(\theta+\alpha)]\,d\theta = 0, \tag{8}$$

$$\int_{\theta_0}^{\theta_1} [-p\cos(\theta+\alpha)+f\sin(\theta+\alpha)]a\,d\theta = W, \tag{9}$$

$$\int_{\theta_0}^{\theta_1} fa^2\,d\theta = M. \tag{10}$$

Equations (6)–(10) contain the whole theory of the film lubrication of the journal bearing, and if U, W, M, a, and μ are known, then the values of δ, c, α, and θ' should be calculable. The difficulty is that the complete solution of equations (8), (9), and (10) in a suitable form would be extremely complex and laborious.

To avoid some of the complexity Reynolds adopted a special device which, however, only held good for values of c up to 0·6, i.e. for conditions in which the eccentricity was only slightly more than half the difference of radii of the journal and bearing. Reynolds did not regard this limitation as serious, because the theory showed that, at some point on the 'off' side of the point of nearest approach, the pressure in the film would become negative (the breakdown of the film under these conditions, owing to the inability of the lubricant to withstand tensile forces, has since been demonstrated by Hyde in experiments with a glass bearing); and that in a semi-cylindrical bearing this negative pressure was to be expected when the eccentricity reached 0·5. Reynolds concluded, therefore, that the limit of safe loading would be reached under this condition.

As it happened, Beauchamp Tower's experiments had been limited to loads and speeds for which the eccentricity went little beyond 0·5, so that Reynolds analysis applied satisfactorily. But Tower's experiments were made with a bearing which subtended about 170° at the journal centre, and the limits in regard to eccentricity without film rupture are fundamentally altered (as Reynolds, of course, recognized) if the arc subtended by the bearing is cut down. By working with very small arcs of contact between the bearing and journal, Stanton [13, 1922] was able to maintain steady film conditions with an eccentricity of more than 0·998, and pressures in the oil film up to 3½ tons per sq. in., i.e. more than 10 times the maximum reached in Beauchamp Tower's experiments. It was Sommerfeld [12, 1904] who devised a method of integration of the equations of the journal bearing free from the limitations of Reynolds treatment, so that conditions of running with eccentricities as great as those in Stanton's experiments could be dealt with.

Stanton's experiments were not actually carried out with a bearing of very short peripheral length, but the equivalent conditions were arrived at by employing a shaft and bearing with a comparatively large difference of radii. The state of things was as illustrated in Fig. 6, in which the curve gives a typical set of pressure readings in the oil film at 1° intervals between the 'on' and the 'off' side. The whole angle subtended by the film was 15° only.

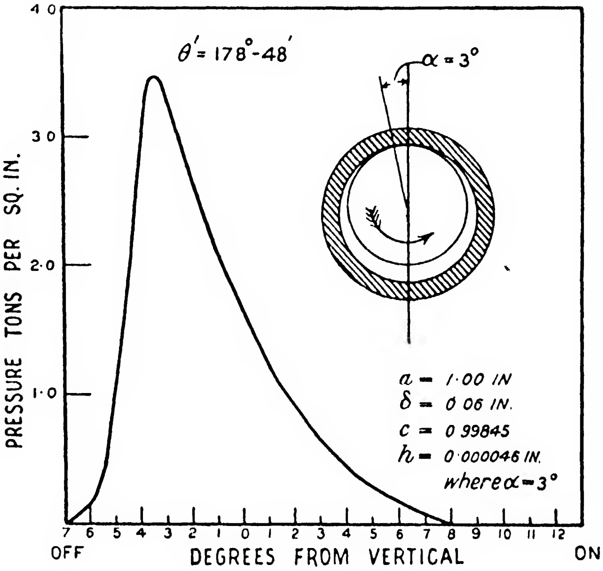


Fig. 6.

In Table I, taken from Stanton's paper, are shown comparative figures for the pressure, eccentricity, and minimum thickness of the oil film, calculated from the data of his experiments, together with a typical case of one of Tower's experiments reduced by Osborne Reynolds. It will be noticed that the minimum thickness of the film in three of the N.P.L. experiments was round about 0·00005 in., and Stanton suggested that this may indicate a possible limit

TABLE I

Experiment	*Diameter (in.)*		*Lubricant*	*Viscosity at observed temp. of oil film and at atmospheric pressure c.g.s. units*	*Load lb. per in. run*	*Relative velocity of surfaces f.p.s.*	*Max. pressure lb. per sq. in.*	*Nominal coeff. of friction*	*Estimated angular position rel. to vertical through journal centre*		*Eccentricity of bearing (calc.)*	*Least distance apart of surfaces (in.)*
	Journal	*Bearing*							*Point of nearest approach*	*Point of max. pressure*		
Tower	4·0	4·003 (calc.)	olive	. .	1,452	15·7	625	0·0013	42·0°	7·0°	0·5200	0·000720
N.P.L.	1·0	1·02	sperm	0·252	277	4·36	3,230	0·0007	6·0°	3°–15′	0·9946	0·000054
N.P.L.	1·0	1·02	rape	0·540	277	4·36	3,190	0·0017	7·0°	3°–24′	0·9904	0·000096
N.P.L.	1·0	1·06	castor	1·43	277	4·36	7,840	0·0023	3·0°	1°–48′	0·99845	0·000046
N.P.L.	1·0	1·06	F.F.F. cylinder (mineral)	2·09	277	4·36	6,250	0·0035	3°–15′	1°–15′	0·9978	0·000066

to the width of a channel in which hydrodynamical flow of a liquid is possible. If one takes the linear dimensions of an oil molecule to be of the order of 10^{-8} in., then a film of the above thickness would contain 4,000–5,000 molecules. This is still a long way off boundary lubrication, and a comparison of experiments 4 and 5 in Table I shows that the nominal coefficients of friction were still closely proportional to the viscosities of the oils at the film temperature, and were unaffected by their chemical natures. This led Stanton to conclude that in a cylindrical bearing the conditions of sustained lubrication are always of the Reynolds type, right up to the point of seizure: a view which is supported by subsequent observations that the maintenance of lubrication in such a bearing at very high temperatures (*c.* 300° C.) and with very low coefficients of friction is dependent upon an extremely high degree of finish of the surfaces of the journal and bush; and that mineral lubricants will stand more extreme conditions and give lower friction, in these circumstances, than the fatty oils, although the latter are superior under boundary conditions.

Definite evidence as to the influence of chemical composition upon the coefficient of friction with films so thin as to approach the boundary condition has been obtained at the Bureau of Standards [3, 1932] with a machine in which three steel rollers are made to slide (not roll) over a flat surface. In the normal region of film lubrication, where no characteristic of the oil except viscosity affects the observed coefficient of friction, the results for oils of widely different types and viscosities when plotted against the product (viscosity × speed) all fall upon a single curve. Even in the thin film region which is reached with the type of apparatus referred to above the coefficients of friction for a series of mineral oils was found to depend only on this product, as is illustrated in Fig. 7, but over the same range of values of the viscosity × speed it will be seen that the castor and lard oils show coefficients of friction varying in a similar manner, but each substantially lower than for the mineral oils. The upper curve in Fig. 7 covers a large number of observations on 4 mineral oils which varied in viscosity between 41·7 and 9,340 centipoises at 25° C.

It will be seen that the coefficients of friction fall in the range 0·1–0·2, and are related, therefore, with those found in boundary conditions rather than in film lubrication, where the coefficients are more in the neighbourhood of 0·01. We may suppose that unevenness of the track passed over by the sliding rollers produced an alternating succession of states in which boundary lubrication is approached, and then relieved by the interposition of a very thin film; and that the observed coefficient of friction is an average result in which the relation of the two surfaces under boundary conditions plays a dominant part.

Although true boundary lubrication plays only a small part in the normal lubrication of machinery, yet this borderline, or alternating, state is to be met with in all toothed gearing, as has been demonstrated by an experiment referred to below. For this, among other reasons, the present discussion would be incomplete without some account of the phenomena of true boundary lubrication. The two primary films with which it deals are always there, and although their reactions with one another may only occasionally become critical, nevertheless it is ultimately upon their behaviour to one another that the danger of a seizure depends. Another reason for the study of boundary conditions, although less practical, is perhaps no less important. In all the vast number of experiments of all kinds which have been made upon the lubrication of machinery, an outstanding fact is the difficulty of achieving a close repeatability. It arises from the complexity of the controlling conditions and of the chemical nature of the average oils of commerce. The result is that almost all the experiments upon what may be called an engineering scale have led to generalizations which show here and there exceptions and inconsistencies.

Unlike this state of things, the theory of boundary lubrication has been built up on the use of pure chemical substances; the conditions of the experiments can be minutely defined; and the results are numerically exact, and repeatable to within the very close limits of accuracy of the observations. The theory, as a result, is no more assailable than the other conceptions of molecular physics, and it forms a really solid foundation upon which our ideas of the behaviour of lubricants in practice should be built up. Moreover, there are some results of great practical importance which can only be explained by a knowledge of boundary conditions.

As a preliminary to describing some of the exact experiments of Hardy and his co-workers, it will be advisable to outline some of the ideas upon which their interpretation is based. The primary films adsorbed on the solid surfaces, on which the coefficient of friction under boundary conditions depends, are composed of oil molecules, and it is first necessary to have a mental picture of what these are like. Although we cannot observe them directly the methods of the chemist, aided by those of X-rays and electron diffraction, have told us almost as much about their form and behaviour as if we could see them. They are built up of straight hydrocarbon chains, or of these chains associated with similar hydrocarbon groups joined together in various types of ring formation. Fig. 8 is from a photograph of a true-to-scale model of a simple hydrocarbon chain of the paraffin series magnified 165 million times. The model is 15 in. long. Notice the carbon atoms represented by the larger spheres, related to one another in a zigzag pattern, each, except the end ones, with two hydrogen atoms attached on alternate sides. This simple chain is symmetrical, end-for-end, and the ends are composed of (CH_3) groups which are relatively stable and inactive. The molecule is illustrated diagrammatically at (*a*) of Fig. 9. Some molecules have chains which end in the hydroxyl (OH) or carboxyl (COOH) groups, and the molecules are rendered chemically active by these less stable end groups. The molecule of palmitic acid, for example, has the stable (CH_3) group at one end and the chemically active (COOH) group at the other. The straight chain contains 16 carbon atoms, and according to the measurements of Langmuir [7, 1917] it has a length of 24×10^{-8} cm. and a breadth about $\frac{1}{8}$ of this. Palmitic acid is an excellent lubricant under boundary conditions. It improves the 'oiliness' of any oil to which a small quantity is added. The molecule of ricinoleic acid, which is present in castor oil, is shown diagrammatically at (*b*) of Fig. 9. This molecule, besides having the carboxyl group at one end, has two other points in the carbon chain at which the chemical valencies of the carbon atoms are unsatisfied, and where, in consequence, the molecule shows an increased tendency to chemical activity. These are the positions of the 'double bonds'.

In each of these fatty-acid molecules the hydrocarbon chain is loaded at one end, as it were, by a group in which the chief chemical activity of the molecule resides. When a molecule is rendered unsymmetrical by having chemically active groups at one end it is characterized as 'polar'. It

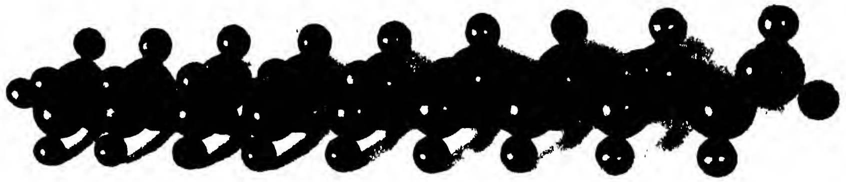


FIG. 8. Model showing special relationship of atoms in a straight-chain paraffin molecule

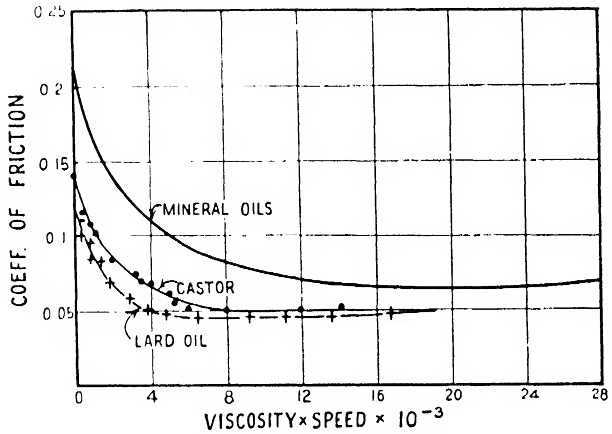
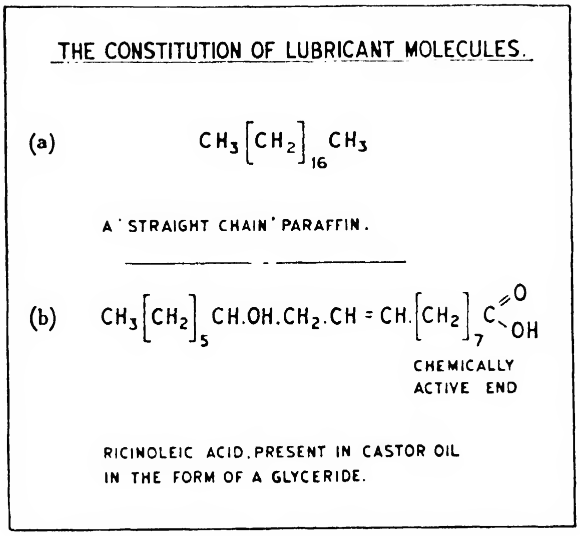


FIG. 7. Coefficients of friction for mineral oils and two fatty oils under conditions of thin film lubrication



THE CONSTITUTION OF LUBRICANT MOLECULES.

(a) $CH_3[CH_2]_{16}CH_3$

A 'STRAIGHT CHAIN' PARAFFIN.

(b) $CH_3[CH_2]_5CH.OH.CH_2.CH=CH.[CH_2]_7C\begin{matrix}{}^{\nearrow\!\!\!\nearrow}O\\{}_{\searrow}OH\end{matrix}$

CHEMICALLY ACTIVE END

RICINOLEIC ACID, PRESENT IN CASTOR OIL IN THE FORM OF A GLYCERIDE.

FIG. 9

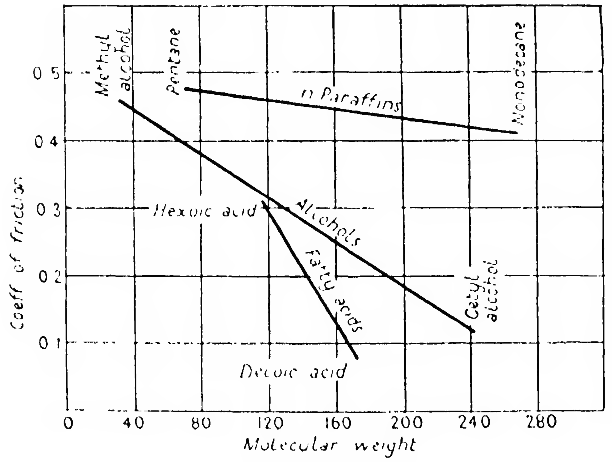


FIG. 11. Relation between coefficients of friction (for steel-on-steel) and molecular weights of certain pure chemical substances used as lubricants

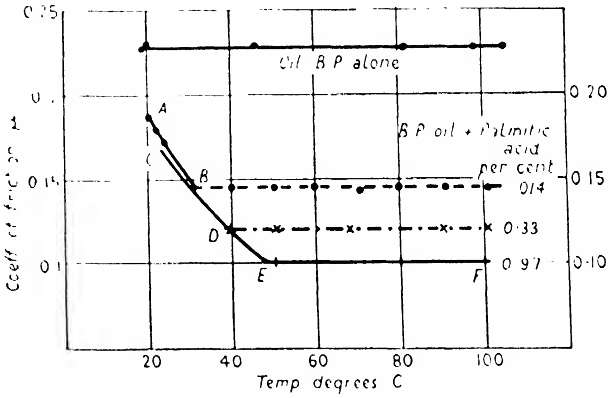


FIG. 12. Friction-temperature curves for paraffin oil B.P. and for the same oil with additions of palmitic acid

has been found that the substances which are the best lubricants under boundary conditions all contain molecules of this polar character, that is, they are of a type in which the end-groups of the hydrocarbon chain are different, one being chemically inactive and the other active. The condition of two neighbouring solid surfaces each carrying a monomolecular layer of polar molecules may be imagined as being something like Fig. 10, in which the small circles, as at *C*, represent the strongly adsorbed ends of the polar molecules and the straight parts, as at *D*, represent the inactive hydrocarbon chains.

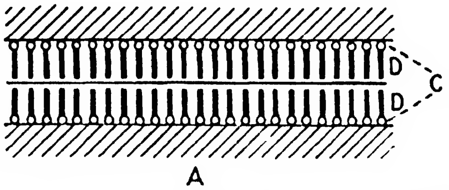


FIG. 10. Polar molecules oriented on a solid surface.

In any attempt to measure the friction between two surfaces in a true state of boundary lubrication the first essential is to obtain the surfaces in an absolutely clean condition, and the second is to be sure that the surfaces are separated only by their primary films and not by a free film of lubricant of finite thickness. The starting friction between two clean dry surfaces under a given normal pressure can be reduced to less than half by a layer of lubricant one molecule in thickness, so that quite invisible traces of any foreign matter will completely upset the observations, and it has been the failure to start with chemically clean surfaces which has led to so many discrepancies between lubrication experiments in the past.

When once the surfaces *are* clean, extremely interesting and consistent results are obtained. A spherically shaped slider, loaded and resting on a plane surface, will at once sink through a pool of oil until the spherical and flat surfaces are separated at their very minute area of contact only by the primary films attached to each. Hardy [4], using such a slider and measuring the friction by the horizontal pull necessary to start the slider from rest, experimented with a number of pure chemical substances as lubricants, in conjunction with sliders and plates of different materials, glass, steel, bismuth, &c. He first showed that the coefficient of friction is truly independent of the load when this is above a small limiting value, and then observed the coefficients for three series of organic compounds. Although many of these would not ordinarily be regarded as lubricants at all, the experiments showed that they did in fact behave as such, and that their properties were exactly related to their molecular weights.

Only the results for a steel plate and slider are given in Fig. 11, but these are typical in character for all the materials used. The three straight lines show how the coefficient of friction was found to vary for each series of chemical compounds in an exactly linear manner with the molecular weight. The three series of liquids used were

(*a*) paraffins, of general formula C_nH_{2n+2} between C_5H_{12} and $C_{19}H_{40}$;
(*b*) alcohols, of general formula $C_nH_{2n+2}O$ between $CH_3(OH)$ and $C_{16}H_{33}(OH)$;
(*c*) acids, of general formula $C_nH_{2n}O_2$ between $C_5H_{11}(CO\cdot OH)$ and $C_9H_{19}(CO\cdot OH)$.

It will be seen that the symmetrical and non-polar paraffins show the highest coefficients of friction, and the least variation with molecular weight. The molecules of the alcohols and acids contain the active (OH) and (COOH) groups respectively, and, of the two, the acids are the more chemically active and hence the more ready to orient themselves in a regular manner on the solid surface. The coefficients of friction are correspondingly lower for the more strongly polar molecules of the acids, and these show, moreover, so rapid a fall with molecular weight that at a value of about 190 the coefficient should be zero. The straight lines indicate that in each series a molecular weight can be reached above which the friction is zero, and experiment showed that in those circumstances the smallest tractive force that could be applied did in fact always produce a slow slip.

A change of the material of the slider and plate had not the smallest effect upon the slope of the line for any one type of compound, but shifted it bodily up or down by a definite amount.

The coefficient of friction can be completely expressed in the form

$$\mu = b-d-c(N-2),$$

in which *b* depends only upon the nature of the solids of which the slider and plate are made; *d* depends only on the chemical series to which the lubricant belongs; *N* is the number of carbon atoms in the chain, and *c* is the decrement of the friction due to each carbon atom, which depends upon the chemical series. It will be noticed that the expression for μ contains no temperature term, for as soon as boundary lubrication with a pure substance is established the force of friction is found to be entirely unaffected by temperature over the range explored, namely, from about 15° to 106° C.

Other striking facts observed when a state of boundary lubrication has been established are: that with a given lubricant the friction is the same whether the temperature is above or below its melting-point; that for any given chemical series the straight lines relating μ with the molecular weight, as in Fig. 11, show no change in direction when increase of the molecular weight alters the lubricant, at a given temperature, from a fluid to a solid; and that when the friction between two initially clean surfaces is measured in a closed vessel containing only the *vapour* of a lubricant, the reduction of friction below the clean surface value is proportional to the vapour density in the containing vessel. It may fairly be argued that the number of adsorbed molecules on the solid surfaces will be proportional to the vapour density, and hence that when the vapour of a lubricant is allowed gradually to condense upon the clean surfaces of the slider and plate each molecule contributes independently to the reduction of the resistance to motion. Finally, it has been shown that the value of the friction obtained between the slider and plate when the primary film has been allowed to form from an atmosphere of the *saturated* vapour is identical with that observed when the slider is standing in a pool of the liquid lubricant. We have here, therefore, very strong evidence that the full reduction of friction below the clean surface value can be obtained by a primary film only one molecule thick.

So long as the force of friction depends upon the viscosity within a fluid film of finite thickness it must, of course, vary considerably with the temperature, and the existence of a state in which friction is independent of temperature is therefore a crucial test that a condition of boundary lubrication exists.

There may, however, be a condition of boundary friction without independence of temperature if the lubricant is not a single chemical substance but a mixture of different molecules, and some most important practical deductions can be made from observations upon simple mixtures of lubricants.

The horizontal line near the top of Fig. 12 shows the observed values of the coefficient of friction, μ, under boundary conditions between 20° and 106° C. for the steel slider and plate when lubricated by the familiar colourless medicinal paraffin oil. This oil, for medical purposes, is rendered as completely inert as possible from the chemical point of view, by the extraction of all the unsaturated and otherwise active elements. From what has been said above it will be understood that a complete removal of unsaturated and polar molecules would reduce the lubricating value of an oil under boundary conditions to a minimum, through the loss of all those components which are strongly adsorbed, and hence that the addition to such an oil of a second, consisting of strongly polar molecules, might be expected to produce a fall in the observed coefficient of friction.

Palmitic acid is a fatty acid with a strongly polar molecule of molecular weight 256 and composition

$$C_{15}H_{31}CO{\cdot}OH.$$

It is one of the substances above the critical molecular weight at which the straight line for its series (see Fig. 11) would cut the axis of zero friction, and when experimenting with it Hardy did, in fact, find that the smallest force he could apply to the slider produced a slow movement.

The lower curves in Fig. 12 exhibit the observed effect upon μ of small additions of palmitic acid—no more than 0·014%, 0·33%, and 0·97%—to the normal B.P.* paraffin. It will be seen that above temperatures ranging from 30° to 50° C. μ becomes independent of the temperature at a value very substantially below the value 0·23 observed with the B.P. oil alone.

Now palmitic acid is a solid with a melting-point at 63° C., and at room temperature it is not readily soluble in B.P. oil. The curves show that a condition of equilibrium is reached at a certain temperature, above which the friction is constant, and that up to additions of 0·97% the maximum lowering of the friction depends upon the amount of palmitic acid added. Higher amounts were tried, up to 6%, but the curves obtained were identical with that for 0·97%.

The temperature ranges of falling friction, *AB* and *CDE* on the curves, clearly represent a series of conditions in which the palmitic acid is becoming more and more dominant in the boundary layer, owing to its increasing solubility in the oil with rise of temperature and to its readiness to form an adsorbed film which displaces the non-polar B.P. oil. At an addition of 0·97% complete solubility is only reached near the melting-point of the acid. At lower percentages complete solubility, and a constant composition of the adsorbed layer, is reached at lower temperatures, but the concentration of palmitic acid molecules is not sufficient to produce the full effect in lowering the observed friction. We may suppose that at 0·97% the acid is sufficient to monopolize the primary film completely, to the exclusion of all non-polar molecules, and thereafter further additions of acid give curves identical with *CEF.*

A close counterpart of these results in the sphere of practical engineering is to be found in the improvement of the lubricating qualities of mineral oils obtained through the addition of small quantities of a fatty acid. This effect was clearly demonstrated by Hyde [6, 1921] in experiments on an engineering scale at the National Physical Laboratory using a worm-gear testing machine. This machine enabled an accurate measure to be made of the efficiency of a set of worm-gears while transmitting power at different known temperatures. The gear-teeth operated under very heavy loads and with mixed conditions of boundary and viscous friction. The proportion of the power being wasted in boundary friction was sufficient to show a 10% reduction of the total loss when 0·2% of oleic acid was added to a straight mineral oil.

The curves of efficiency for the gear, and of a calculated mean coefficient of friction, between 25° and 75° C. are shown in Fig. 13. The addition of 0·2% of acid produced an increase of about 0·4% in the efficiency throughout the temperature range, while adding 10 times that amount produced only a further 0·2% in the efficiency.

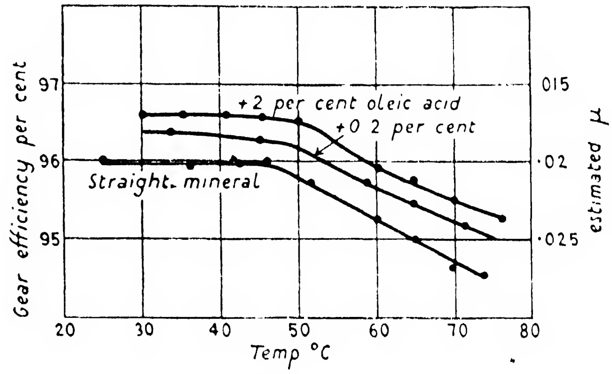


FIG. 13. Efficiency-temperature curves for Lanchester worm-gear machine with a straight mineral oil and with the same oil plus additions of oleic acid.

The fall of efficiency and increase of friction with temperature is no doubt to be explained by the fact that as the oil became less viscous it was more rapidly squeezed out from between the gear-teeth, so that a larger and larger proportion of the normal forces between the gear surfaces were being carried by very thin films, approximating at times to the ultimate primary films giving boundary friction. The increase of friction from this cause would more than balance some reduction of the loss due to viscous friction, for it must be remembered that the average coefficients of friction obtained with fluid film lubrication are no more than about 1/10 of those for boundary friction, even with the best lubricants.

It is not possible to give definite figures for the coefficients of kinetic friction between two primary films. Hardy's observations were all upon the force necessary to start his slider from rest, and they yield, therefore, coefficients of static friction. The lower limit of μ for a mineral oil in these static experiments may be taken as being roughly 0·1, but there is evidence of a fall in the friction as soon as movement occurs (cf. Fig. 7). The most likely thing appears to be that under kinetic conditions the slipping over one another of the real primary monomolecular layers ceases to hold, and that the friction rapidly develops into that produced by the slipping of layers several molecules thick, the outer layers being oriented in a more or less orderly manner when the molecules of the lubricant are strongly polar, but not so firmly held by the chemical bonds of the solid surface as the strongly adsorbed primary layers. Under kinetic conditions, therefore, the physical state of

---

* Prepared according to the British Pharmacopoeia.

the surfaces is altered, and can be less completely defined than in Hardy's static experiments. Boundary friction under kinetic conditions will shade off into fluid film lubrication without any clear line of demarcation between the two.

In the worm-gear experiments represented in Fig. 13 the load is transmitted nominally at line contacts, and one would expect films of all thicknesses down to a very few molecules, and an approach, therefore, to boundary conditions, at the points where the load is concentrated. This is borne out by the value of the estimated average coefficient of friction for the gear, 0·020 to 0·027 for the straight mineral oil (see Fig. 13) which is substantially higher than it would be if it depended on fluid friction, although only about $\frac{1}{5}$ of the value for static boundary conditions.

There can be little doubt that the lowering of the apparent coefficient of friction by about 0·002 in the worm-gear testing machine when 0·2% of oleic acid was added to the mineral oil is to be explained by surface changes of the same kind as those when the static coefficient in Fig. 12 was lowered from 0·23 to 0·10 by the addition of 0·97% of palmitic acid. In each case the 'oiliness', or lubricating property under boundary conditions, of a non-polar oil was substantially improved by the addition of a very small proportion of polar molecules. These form strongly adsorbed primary layers on the solid surfaces, displacing the non-polar molecules and reducing the coefficient of friction accordingly.

REFERENCES

1. Beauchamp Tower. *Proc. Inst. Mech. Engrs.* 1883 and 1885.
2. Boswell. *Proc. Inst. Mech. Engrs.* 1932.
3. Bridgeman, McKee, and Bitner. *Proc. A.P.I.* Dec. 1932.
4. Hardy, W. *D.S. and I.R. Lubrication Research.* Technical paper no. 1 (H.M.S.O. London).
5. Harrison. *Camb. Phil. Soc. Trans.* 39 (1913)
6. Hyde. *Engineering*, 10 June 1921. See also 'Report of Lubricants and Lubrication Inquiry Committee' (H.M.S.O. London, 1920).
7. Langmuir. *J.A.C.S.* **39** (1917).
8. Martin. *Engineering*, **101** and **102**.
9. Michell. *Z. für Math. und Phys.* 123 (1905). See also *The Mechanical Properties of Fluids*, 140 (Blackie, 1923).
10. Osborne Reynolds. *Phil. Trans.* 157 (1886).
11. Rayleigh. *Phil. Mag.* Jan. 1918.
12. Sommerfeld. *Z. für Math. und Phys.* 97 (1904).
13. Stanton. *Proc. Roy. Soc., A*, 241 (1922). See also *Friction* (Longmans, Green & Co., 1923).

CHEMICAL AND PHYSICAL FORCES IN LUBRICATION

By G. L. CLARK, R. R. STERRETT, *University of Illinois*, and Bert H. LINCOLN, *Continental Oil Company, Ponca City, Oklahama*

DURING the past few years more and more attention has been directed by chemists and physicists to the study of lubrication. The former have attempted to determine the relationships existing between the properties of a lubricating oil and its chemical components. The latter have endeavoured to elucidate the mechanism of lubrication. Recent investigations have involved the application of chemistry and physics towards the solution of practical lubrication problems.

The chemical and physical forces involved in boundary lubrication have been treated at great length in the literature, but the subject is not yet perfectly understood. While the theory of viscous lubrication, based on hydro-dynamic laws, is well developed, the action of physico-chemical forces in this connexion has not been fully realized. This article will consider the nature of the forces emanating from metal surfaces and from various types of molecules found in and added to lubricants. An understanding of these forces and their profound influence, under both viscous and boundary conditions, is essential to the fundamental theory of lubrication. We propose to control and direct these physico-chemical forces to the improvement of both types of lubrication. For this purpose the addition of certain chlorinated esters of long-chain fatty acids and short-chain monohydric alcohols serves very satisfactorily [28, 1933–5].

Viscous and Boundary Lubrication

Lubricants are applied to the moving parts of machinery to keep the rubbing surfaces from coming into contact and causing high friction or seizure of the metals. In practical lubrication two distinct types of conditions are encountered. If the rubbing surfaces are completely separated by a comparatively thick film of oil, the lubrication is designated as 'viscous'. If the lubricating film is extremely attenuated, the type of lubrication is referred to as 'boundary', in which case the rubbing surfaces are in approximate contact. The designing engineer aims at perfect viscous lubrication without attaining it, and cannot avoid encountering boundary conditions in the practical use of mechanical devices.

Viscous lubrication is essentially kinetic, and can be realized only when the relative motion of the surfaces is sufficiently great to form a lubricant layer of appreciable thickness between the moving surfaces under suitable conditions of loading, viscosity of oil, temperature, speed, and, to some extent, the nature of the oil. When all of these conditions are satisfied, the friction is due almost entirely to the viscosity of the oil and the physico-chemical attractive forces between the rubbing surfaces and the lubricant. Under viscous-lubrication conditions there can be no metal-to-metal contact; therefore there should be no wear or seizure of the metal surfaces.

In boundary lubrication, friction is independent of the speed (only within certain limits) and is a function of the load and of the chemical and physical relationships between the rubbing surfaces and between the surfaces and the lubricant. Before passing to a discussion of the physics and chemistry of this state, it may be of interest to note that boundary lubrication must appear in all cases where the speed of rubbing is too low, the oil viscosity is too low, or the load is too great to permit the formation and persistence of a thick layer of lubricant.

In engineering practice, boundary-lubrication conditions may obtain:

1. At the moment of starting a machine from rest.
2. During the extreme slowness of the moving parts just immediately prior to stopping.
3. In reciprocating and rocking motions.
4. With rapid fluctuations of speed or load (shock pressure) which tend to bring the metal surfaces momentarily within their range of effective attraction.
5. When the original viscosity of the lubricant is too low or is excessively reduced by heat.
6. With an inadequate supply of oil.

Oiliness

Friction is obtained in both viscous and boundary lubrication. Ewing [17, 1892] was probably the first to realize the factors contributing to friction in boundary lubrication, and Kingsbury [26, 1903; 40, 1919] considered this concept in his early work.

Many subsequent investigators [5–10, 12–14, 16, 20, 22, 27, 29, 33, 35, 37–8, 41–3, 45–6, 48] have contributed to our fund of knowledge of the special character of a lubricant which causes differences in the friction when one lubricant is compared to another of the same viscosity under identical conditions. 'Oiliness' has been conceived as responsible for the difference in friction.

This definition proposed for oiliness is based upon the historical concept as a friction-reducing property only. There is no known established relationship existing between oiliness, wear, and seizure. It does not appear that the terms 'wear' and 'seizure' have yet been satisfactorily defined, or that the elementary factors entering into these phenomena have been systematically investigated. Other things being equal, a lubricant of superior oiliness will develop less heat in use, and to that extent conditions will be favourable for reducing wear and preventing seizure [22, 1933]. By controlling the physical and chemical forces involved in lubrication it is possible to obtain reduced friction (increased oiliness) and also greatly minimize metal loss from rubbing surfaces by wear or seizure.

Friction between smooth, polished surfaces is caused by the unbalanced forces of molecular attraction acting across the interface. By placing a lubricant between the surfaces, these unbalanced forces are completely neutralized in perfect boundary lubrication; while in perfect viscous lubrication the rubbing surfaces are separated by the liquid oil beyond their effective fields of force.

Polar Molecules

Molecules of ordinary hydrocarbon lubricants are not sufficiently physico-chemically active to neutralize the unbalanced forces acting at metal surfaces. However, molecules which contain an atom or group of atoms exhibiting secondary or residual valence—which are known as polar molecules—are able to neutralize these unbalanced forces. This is accomplished by means of the polar groups present in the molecules, which are attracted by the forces of the metal surface resulting in a regular orientation of the molecules with respect to the surface. This ability to orient seems to be an inherent property of polar molecules, given the proper conditions of molecular mobility.

The orienting and adhesive character of polar molecules has been demonstrated by the works of Marcelin [30], Devaux [15, 1904, 1912], Langmuir [27, 1916–17, 1920, 1934], Adam [1, 1922–3, 1930], and Woog [48, 1924–6, 1928]. They show that, in the spreading of organic liquids on water, strong selective forces reveal themselves in a preferred attraction by the water for quite definite atoms or groups of atoms of the organic liquid. Thus, for example, water exerts an especially strong attraction for terminal hydroxyl, carboxyl, and other oxygen-containing groups in organic compounds. By these specific selective forces of attraction, the surface films of organic molecules are anchored to the water substratum.

The same authors have shown entirely analogous relationships in the spreading of liquids on solid surfaces. It has been shown, for example, that the carboxyl group displays an especially strong attraction for metal surfaces. In order to prevent metal-to-metal contact in lubrication, the film must be so firmly bound to the rubbing surfaces that it withstands the action of pressure and shearing forces which seek to crush, tear, or squeeze out the film. By virtue of their active polar groups, certain molecules are not only concentrated at the boundary surface, but are also fixed there by strong forces. This adhesivity of the polar film and the viscosity of the lubricant are in no way related. Karplus [24, 1929] has found that certain non-viscous oils adhere to a definite boundary surface much better than a viscous oil—which has been confirmed by our work.

From the specific nature of the mutually attractive forces between the lubricant and the metal surface, it follows that the strength of the attraction depends not only on the polarity of the lubricant, but also on the physical and chemical nature of the metal surface. The polarity of the lubricant, and the kind and strength of the specific forces of attraction emanating from the metal surface, determine the stability of the adhering film. Long-chain polar molecules are firmly rooted with their polar ends on the rubbing surface, with their free ends projecting into the lubricant layer and their chains parallel.

Film Characteristics

Many have assumed that the effective sphere of action of polar molecules is always very small, i.e. that the mutual attraction of these molecules can act only through small distances. The work of Freundlich and others has made the existence of far-reaching forces of attraction appear plausible. The work of Hardy [20, 1918–20, 1922, 1926, 1928], and his co-workers, on adhesion has proved with certainty that forces of attraction, extending actually through an unexpectedly large circle of action approximating 20,000 Ångström units (Å.U.), emanate from solid boundary surfaces. Kingsbury found that the hydrodynamic laws of viscous lubrication apply to a film as thin as 6,250 Å.U. (vide Hersey [22, 1933]). The molecular forces of attraction which originate in the solid boundary surfaces are thus not limited to the layer in direct contact with the metal, but are extended far into the interior of the lubricant layer. Trillat [43, 1926–8] has found such powerful fields of attraction between metals and polar compounds that laminated structures of 400–500 molecular layers are formed, which in the case of long-chain fatty acids would give a film thickness of 9,000 Å.U. or more. Tausz and Szekely [41, 1930, 1933], by capacitance methods, have shown films of 12,000 Å.U. thickness with non-polar compounds which ruptured under stress, but polar films as low as 1,100 Å.U. thickness which did not rupture under the same conditions. Therefore it is seen that three independent investigators have found film thicknesses of comparable magnitude.

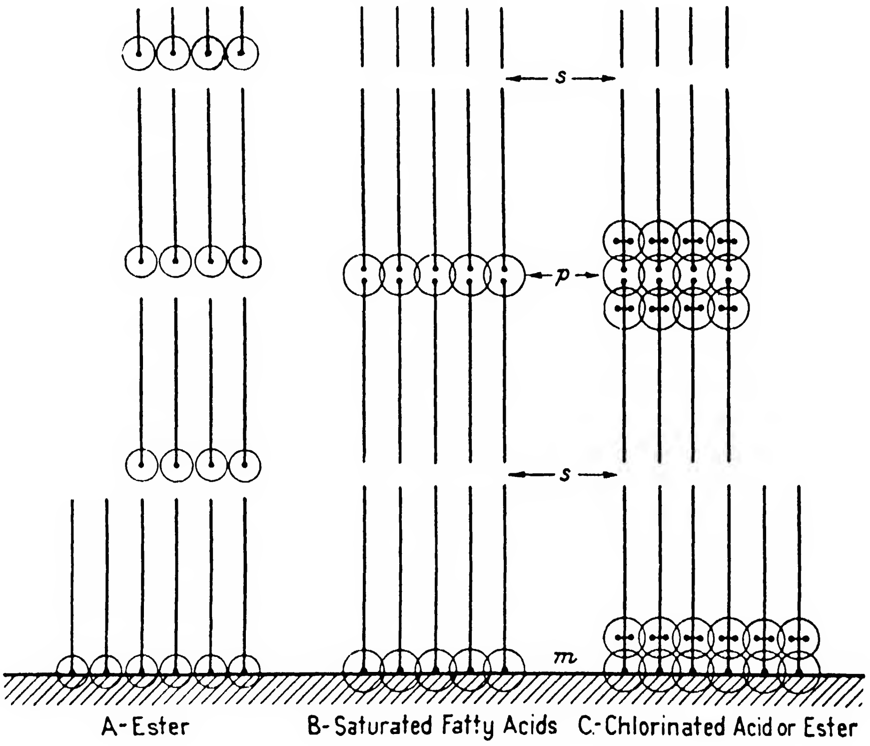


FIG. 1.

Karplus [24, 1929] concluded that the forces of attraction act between the metal surface and the polar groups in the lubricant to form an oriented film, as represented in Fig. 1, and to determine the resistance to separation of the adhering film from the metal surface. The forces of attraction which bind the hydrocarbon chains to each other (as will be discussed later in connexion with Fig. 1 B), in terms of the work necessary to separate them, were calculated from the approximate molar-cohesion values of Meyer [31, 1928], and amount, for example, to about 17,000 calories for an unsubstituted fatty acid of 18 carbon atoms. These forces of attraction are determining factors for the pressure stability of the film, i.e. for the resistance which the lubricant layer sets up against the forces acting perpendicularly to the solid boundary surfaces. The work necessary to separate the carboxyl planes amounts to about 9,000 calories per gram-mol for unsubstituted fatty acids, and more in acids in which hydrogen close to the carboxyl group has been substituted by strongly polar atoms or groups of atoms. To overcome the forces in the cleavage or methyl plane requires only about 1,790 calories per gram-mol. This explains the outstanding sliding capacity of the lubricant along the cleavage plane.

Physico-Chemical Forces in Viscous Lubrication

Herschel [21, 1923, 1929] has emphasized the influence of the oil, and particularly of the bearing metal, on the coefficient of friction. He shows that this is a joint property of the oil and the metal forming the rubbing surfaces.

Becker [6, 1926] recognized the early interest in surface action between lubricants and metals as it pertains to boundary lubrication, and stated that the influence of surface forces is also of vital importance in viscous lubrication. He concluded: 'Thus the thickness of film developed in a bearing depends upon the speed, load, viscosity of the lubricant at the working temperature, and upon four constants—the latter being dependent upon the oil and the bearing surfaces used. In other words, surface action plays a very important part in the development of viscous lubrication. . . . These experiments demonstrate, therefore, that the thickness of oil film developed in a given bearing under definite operating conditions depends on surface action as well as viscosity.'

Gilson [19, 1928] shows that the kind of metal in the rubbing surfaces has a strong influence on the coefficient of friction. His work was done with a set of bearings operated under conditions to give as nearly perfect viscous lubrication as is possible to obtain. Viscous lubrication was obtained in these experiments by a speed of 2,000 r.p.m., a load of only 10 lb. per sq. in. of projected bearing area, and an abundant oil supply. All variable factors, except composition of bearing surfaces, were kept constant. Varying the composition of metal surfaces gave differences in coefficient of friction of 53%. This is contrary to the hydrodynamic theory of viscous lubrication, which says that under constant load and speed the only factor affecting the coefficient of friction is the viscosity, i.e. that the coefficient of friction should always be entirely independent of the kind of metal in bearing surfaces.

Since the coefficient of friction in viscous lubrication does vary with the type of metal in the rubbing surfaces, the magnitude of the fields of force around the metal surface must play an important part. Obviously, ordinary non-polar lubricants do not saturate these fields of force to allow a constant coefficient of friction with constant viscosity. We find that strongly polar compounds in a lubricant, such as the chlorinated esters, do neutralize these fields of force. Furthermore, the X-ray evidence presented later will show that such polar compounds as the chlorinated esters actually produce a more or less complete regimentation of the molecules in the liquid body of the lubricant between the rubbing surfaces. This regimentation, or 'cybotaxis', is sufficiently strong that the disturbing influence of temperature increase—which tends toward a chaotic molecular arrangement—has little or no effect for reasonable increments of temperature. This arrangement gives the cleavage planes which promote sliding and, thus, tend to reduce friction.

The neutralization of the fields of force of rubbing surfaces by polar molecules and the regimentation of the molecules in the liquid lubricant may explain, in part, the above anomalous coefficients of friction in viscous lubrication.

The physico-chemical activity at the rubbing surface in boundary lubrication, and in the liquid body in viscous lubrication, may be different in degree, but not in kind. This particular phase of viscous lubrication is being further investigated.

Physico-Chemical Forces in Boundary Lubrication

As there is no simple and direct method of measuring the physico-chemical forces under conditions of boundary lubrication, many devices and methods have been developed to study the effects of such forces. Probably the most commonly used are the various methods of determining the coefficient of friction under boundary conditions. These measure the oiliness of lubricants and, therefore, give methods of directly comparing film-forming properties of polar compounds in lubricants.

Oiliness can be measured in any device capable of being loaded to thin-film conditions and equipped to measure friction or resistance to motion. Friction is measured under two conditions: 'static', which is the resistance to starting of stationary surfaces; and 'kinetic', which is the resistance to motion of moving surfaces.

Hardy's [20, 1918, 1919–20, 1922, 1926, 1928] method for static coefficient of friction, with its slider and inclined plane which can be set at varying angles, has been widely used by investigators. Table I shows some of our results by this method. The value given for each series is an average of 30 tests. The plane and balls were thoroughly cleaned with petroleum ether and alcohol between each series of determinations shown in the table. The check determinations shown in the first part of the table were made without changing the contact surfaces, but the surfaces were changed between each check shown in the second part of the table. Our experience has shown that the degree of polish and cleanliness of the bearing surface has a great influence on the results.

TABLE I

Static Coefficient of Friction by Inclined Plane

Series	*Addition agent*	*Average coefficient of friction*	*Decrease (%)*
	Without changing surfaces for check tests:		
1	None (mineral oil) . .	0·255	. .
2	1% chlorinated ester . .	0·226	11·4
3	0·5% oleic acid . . .	0·207	18·8
	Changing surfaces for check tests:		
4	None (mineral oil) . .	0·275	. .
5	1% chlorinated ester . .	0·246	10·5
6	0·5% oleic acid . . .	0·209	24·0

The Almen machine [47, 1932] may be used to obtain the static coefficient of friction by determining the 'break-away' torque or the force required to start rotation. Table II compares the static coefficient of friction as determined with the Almen machine (steel-to-steel) for an S.A.E.–30 mineral oil, and the same product blended with 0·75% methyldichlorostearate and with 0·5% oleic acid, respectively.

TABLE II

Static Coefficient of Friction with Almen Machine

	Coefficient of friction	*Decrease (%)*
Mineral oil, S.A.E.–30	0·215	. .
Oil plus 0·75% chlorinated ester . .	0·194	10
Oil plus 0·5% oleic acid . . .	0·200	7

We have found a simple modification of the Almen machine to be of value in the chemical laboratory in showing the relative oiliness of various compounds. This hand-operated device uses a steel split bushing and a brass pin as rubbing surfaces and a spring-loaded torque scale. Under a load of 3,000 lb. per sq. in. of projected bearing area, the starting torque with a mineral oil and with a given compound in the same oil is determined. The reduction of the torque of the mineral oil by a number of compounds compared with their Timken film strength is given in Table III.

TABLE III

Effect of Polar Compounds on Starting Torque

No.	*Compound added*	*Timken film strength (lb.)*	*Decrease in torque (%)*
1	Trichlororesorcinol . .	125·0	74·1
2	Methyldichlorostearate . .	28·0	60·9
3	Chlorostearic acid . . .	64·0	20·0
4	Ethyldichlorophthalate . .	38·0	24·0
5	Trichloroanisole . . .	13·8	30·4
6	Oleic acid	10·3	33·3
7	Hexyl chloride . . .	8·8	4·5*
8	*o*-Chlorophenetole . . .	14·8	8·0*

* Increase.

From the table it will be noted that there is no direct relationship between film strength and oiliness as measured by starting torque. The presence of an element such as chlorine in the molecule does not necessarily decrease the torque. Since the torque varies with the load and metals used, this test is of value to indicate trends rather than absolute values.

Measurement of Kinetic Coefficient of Friction

The measurement of the kinetic coefficient of friction may be determined on the Herschel machine [21, 1923, 1929]. Table IV gives the coefficient of friction between steel and various metals when using an S.A.E.–30 mineral oil and the same oil blended with 0·5% oleic acid. It will be seen that there is a wide difference in the coefficient of friction obtained by the polar oleic acid on the different metals.

TABLE IV

Effect of Metal on the Kinetic Coefficient of Friction

Bearing surfaces—steel on:	*Coefficient of friction*		*Decrease (%)*
	Mineral oil	*Oil with 0·5% oleic acid*	
Tin babbitt	0·150	0·101	33
Cadmium silver . . .	0·097	0·110	11*
High lead	0·162	0·094	42
Phosphor bronze . . .	0·173	0·176	2*
Copper lead (1) . . .	0·136	0·126	7
„ (2) . . .	0·154	0·145	6
No. 1 A.S.T.M. . . .	0·180	0·140	22
Bronze	0·182	0·126	31
Cast iron	0·133	0·122	8

* Increase.

The Almen machine may also be used for measuring the kinetic of coefficient of friction. Table V gives the effect of the load in pounds per square inch of projected area for mineral oil, and the same oil containing 0·75% of methyldichlorostearate with steel-to-bronze surfaces at 1·2 r.p.m. It will be seen that the coefficient decreases slightly with the increase in load. Table VI shows the results obtained by variable speed. The increase in the coefficient of friction with speed under the 1,000 lb. load indicates viscous lubrication. The decrease in the coefficient of friction with speed under the 5,000 lb. load shows the effect of the polar film under conditions of boundary lubrication.

TABLE V

Effect of Load on the Kinetic Coefficient of Friction

Load (lb. per sq. in.)	*Coefficient of friction*		*Decrease (%)*
	Mineral oil	*Oil with 0·75 % chlorinated ester*	
1,000	0·269	0·153	43
2,000	0·288	0·135	53
4,000	0·259	0·134	50
6,000	0·243	0·128	47
8,000	0·240	0·125	48
10,000	seized	0·124	. .

TABLE VI

Effect of Speed on the Kinetic Coefficient of Friction

	Coefficient of friction		
Speed, r.p.m.	0·5	600	1,800
Load – 1,000 lb.:			
Mineral oil	0·230	0·241	0·289
Oil with 0·75% chlorinated ester	0·192	0·192	0·249
Load– 5,000 lb.:			
Mineral oil	0·269	seized	seized
Oil with 0·75% chlorinated ester	0·207	0·162	0·085

Interfacial Tension

Another method of studying the physical and chemical forces in lubrication involves the measurement of interfacial tension between the lubricant and either a metal or water. This may be measured in a number of ways. For example, we employed a drop-weight method for determining interfacial tension between mercury and an S.A.E.–30 mineral oil and the same oil with certain polar addition agents. The capillary was constructed to deliver 5 drops of mercury each 3 min. Check determinations were hard to obtain until the proper technique was developed. The total weight of 100 drops was used to determine the average weight of one droplet. The difference in density of oil and mercury is so great, compared to slight changes in the oil density due to the incorporation of the polar compound, that this variation may be neglected. Table VII shows the results obtained. The decrease in the average drop weight corresponds to a similar decrease in interfacial tension between the oils and mercury.

TABLE VII

Interfacial Tension of Mercury against Oil by Drop-Weight Method

Oil with 5% of:	*Weight of droplet of mercury (g.)*
Mineral oil	0·206
Trichloronaphthalene	0·192
Trichlorophenol	0·191
Oleic acid	0·190
Monochlorodiphenylene oxide	0·186
Methyldichlorostearate	0·186

The interfacial tension between mercury and the various blended oils, even though in favour of the use of addition agents, does not give a complete picture. Different results would be obtained with the same oil blends on other metals because of the differences in the nature and magnitude of the fields of force at the surface of various metals. Since the other metals are not liquid at reasonable working temperatures, this method cannot be employed and is, therefore, of little practical value.

Capacitance Method

Tausz and Szekely [41, 1930, 1933] determined, by capacitance methods, the thinnest film which is stable under certain conditions. Since the imperfections of two highly polished flat metal surfaces prevent uniform separation by a lubricant layer, they used a cleaned, oiled steel ball immersed in clean mercury. They found that very tough thin films could be obtained with polar vegetable oils and lubricants. For example, the films of non-polar oils of less than 5,000 Å.U. would break in two days, while polar oil films 300–1,000 Å.U. in thickness were very resistant and did not break under equal stress for 65 days. The results show that the force with which lubricants are attached to metal surfaces depends on the type of polar molecules present. A good lubricant should contain compounds with such properties, although all polar molecules are not satisfactory as addition agents.

Oil Adhesion

Parrish and Cammen [34, 1932] define 'oiliness' as 'adhesion'; and claim that their 'Adher-O-Scope', by measuring the amount of oil adhering to a metal drum after rotation at high speed, is a measure of this characteristic. Since some metals are permeable by oil as shown by Gill [18, 1935], the Sperry-Cammen tester would not distinguish between the polar affinity of molecular layers and simple absorption of the oil by the metal.

Heat of Wetting

When certain polar liquids are brought into contact with metals, the neutralization of the mutual attraction between the polar molecules and the metal-surface molecules usually results in the evolution of heat. The total heat of wetting is dependent on the total metal surface. Since a solid metal surface does not have sufficient area to give a measurable heat of wetting, a powdered metal is used. The surface area is difficult to determine with any degree of accuracy when a powder is used; hence the data indicate only the relative forces with which the polar molecules attach themselves to metal.

The heat of wetting has been employed to compare the lubricating efficiency of different lubricants. Assuming that this characteristic is a measure of the adhesivity of the lubricant for the metal surface and that no chemical action takes place, then the best lubricants should have the highest heat of wetting. While it would be possible to have a negative value with a positive free energy of wetting, as a rule the heat of wetting runs roughly parallel with the adhesivity—just as the heat of chemical reaction often runs parallel with chemical affinity.

Bachmann and Brieger [3, 1925] studied the heat of wetting obtained by treating certain lubricants with freshly prepared copper powder. Following their technique, we obtained data on additional substances which are shown in Table VIII. The heat of wetting is reported as the number of calories produced per 100 g. of copper for each per centage of the polar compound in the oil, when a sufficient quantity is employed for wetting. Lubricants containing polar compounds show a higher heat of wetting than refined straight-hydrocarbon lubricants.

TABLE VIII

Heat of Wetting of Oils on Powdered Copper

	Heat of wetting in calories	
Polar compound in oil	*Bachmann and Brieger*	*Authors*
Mineral oil	3·8	2·8
Oleic acid	22·0	36·0
Castor oil	12·4	..
Linseed oil	14·4	..
Methyldichlorostearate	..	12·8

All the above methods of investigation pertaining to the effect of physico-chemical forces between polar molecules and metals have contributed to our general knowledge of film lubrication. These methods of test do not give any information whatever concerning the structure and dimensions of the oriented film. We have used X-rays for the study of these films and their characteristics.

X-Ray Investigations of Effects of Physico-Chemical Forces in Lubrication

The early use of X-rays in studying the characteristics of fatty-acid films on metal surfaces led us to the consideration of X-rays for the general study of polar compounds in viscous and boundary lubrication. We found it necessary to develop new methods and new technique of applying X-rays to the problem.

Bragg [9, 1925], Trillat [43, 1926–8], and Mueller and Shearer [32, 1923] observed from X-ray patterns the peculiar properties of fatty-acid films which could be used to account for their beneficial properties when added to a mineral oil. Trillat proved, by making X-ray photographs of fatty acids adsorbed on metal plates, that polar compounds orient directly and spontaneously on metal surfaces.

Fundamental Concepts

In the interpretation of X-ray photographs certain fundamental concepts must be kept in mind. Some polar molecules orient so systematically that their thin-film structure is quite regular—and the entire film behaves as a diffraction grating in the same sense as any single crystal. By analogy with the X-ray study of crystals, similar studies

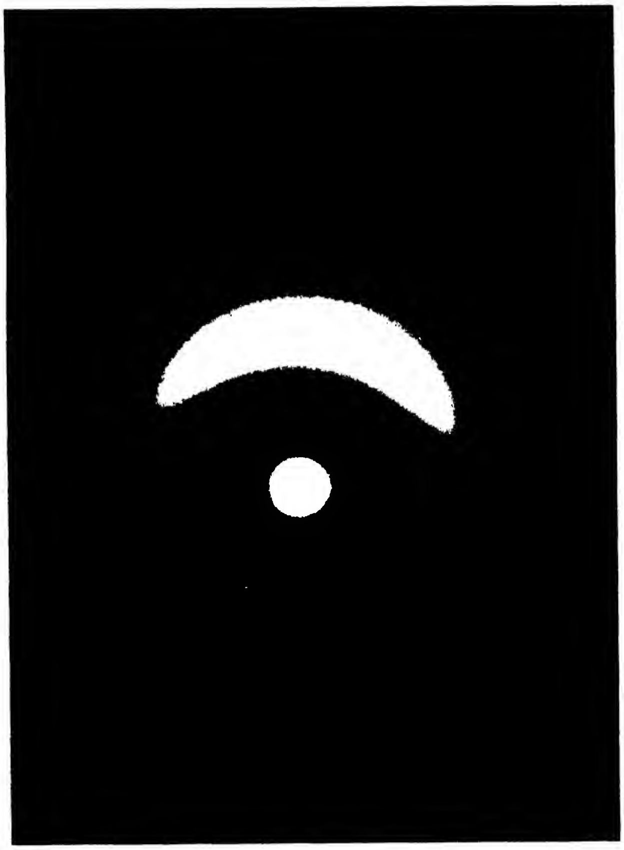


Fig. 4

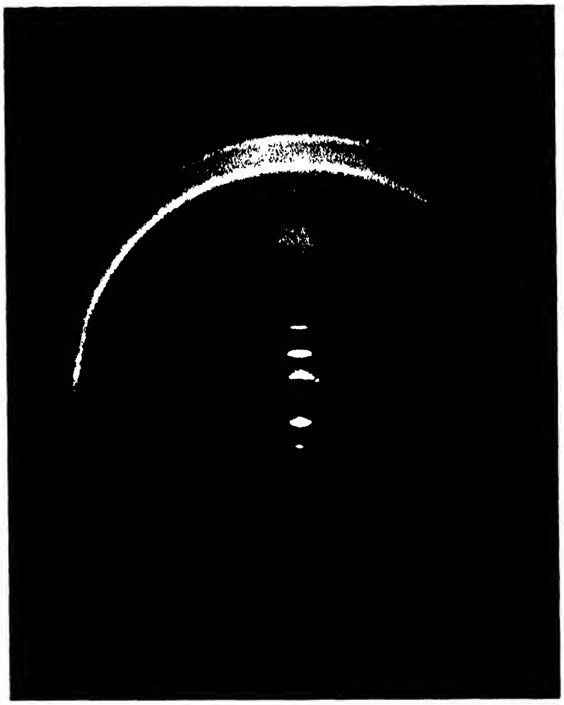


Fig. 5

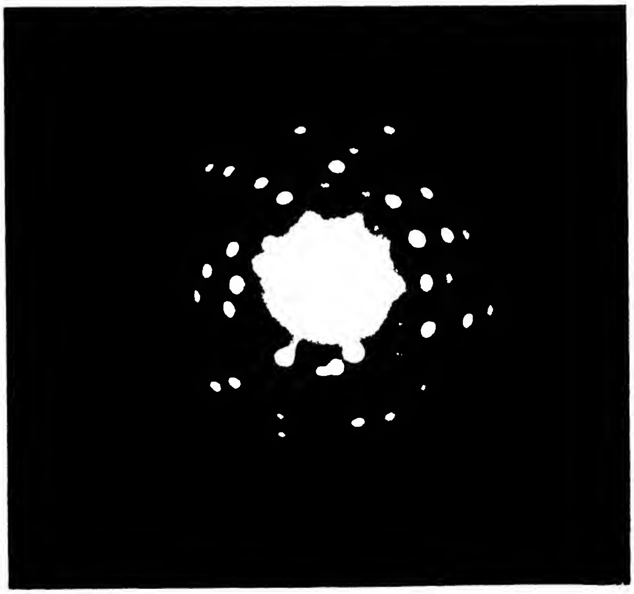


Fig. 3

have demonstrated that these polar molecules orient themselves in definite fashion side by side. The long-chain polar molecules also orient in an end-to-end fashion, the degree of which is measured by the number and shortness of the diffraction arcs. This may be illustrated by a stack of carpets, each carpet representing a parallel plane and the pile of the carpet representing the molecules standing perpendicularly to these planes.

A schematic portrayal of the molecules in the film is shown in Fig. 1. The vertical lines represent the hydrocarbon chains; the dots at the end of the lines the polar groups. The circles are used to designate the interlocking fields of force. In the primary film the polar groups are directed toward, and firmly attached to, the metal surface, *m*, by virtue of their marked affinity for it. The hydrocarbon chains are arranged parallel to one another. When a first layer has been formed on the metal surface, a more or less homogeneous surface is produced by the free ends of the adsorbed molecules, which serves as a foundation for the formation of a second layer of attracted polar molecules. In this way many layers of adsorbed molecules may be formed on a metal surface, although the force which serves to bind the molecular layers decreases progressively as the distance from the surface increases. The polar groups standing opposite each other are bound firmly in consequence of their strong affinity. In the planes of the methyl groups the mutual forces of attraction, as previously shown, are very slight on account of the small affinity between these groups. In these planes, therefore, sliding can result with minimum friction.

The polar compound may act in a number of different ways in building this film. Fig. 1 A shows how a long-chain weakly polar compound, such as methylstearate, builds a film with the polar end of the first layer of molecules attached to the metal surface and all the single molecules in the succeeding layers oriented in the same direction. Molecules of fatty acids, such as stearic acid, orient as shown in Fig. 1 B, with the first layer arranged mono-molecularly on the metal surface like methylstearate. The succeeding layers are built with a double molecular unit, which is formed by the association of two molecules because of the high polarity of the carboxyl groups. These molecular arrangements are referred to as single and double, respectively.

The type of film formed by chlorinated esters is shown in Fig. 1 C. The circles on each of the hydrocarbon chains near the carboxyl end represent the fields of force of the two chlorine atoms on the alpha carbon. These fields of force magnify the total degree of polarity of the molecule. By the introduction of the two chlorine atoms, the weakly-polar methylstearate becomes more active physicochemically than the stearic acid, and displays a double molecular arrangement similar to stearic acid.

If the chlorine atoms are placed on the chain near the middle, they detract from the fields of force around the carboxyl group—and cause the molecule to act quite differently. Probably in this case the long-chain molecule is weakly attached to the metal surface at the carboxyl end and at the point of chlorine introduction, rather than strongly at the carboxyl end only.

The planes, *s*, shown in Fig. 1 B and 1 C are the slippage planes which are not present in Fig. 1 A—because, with the single-molecular arrangement, there is no plane in which the methyl ends of the molecules are in contact. The planes *p*, have the maximum electron-density concentration, and are the diffraction planes for the X-ray beam.

X-Ray Diffraction

The diffraction of an X-ray beam by oriented adsorbed layers on a metal surface is shown diagrammatically in Fig. 2. The planes of diffraction, *p*, are the planes of maximum electron density as shown in Fig. 1. If a monochromatic X-ray beam is passed through the film at the angle θ to the diffraction planes, *p*, the elements of the beam A–A_5 will be in phase at the points of diffraction B–B_5, and will combine to form the diffracted beam, *C*. If there is a sufficient number of molecular layers, the diffracted beam will be built up to sufficient intensity—as indicated by the broadening of the beam to affect a photographic plate placed perpendicularly to the beam.

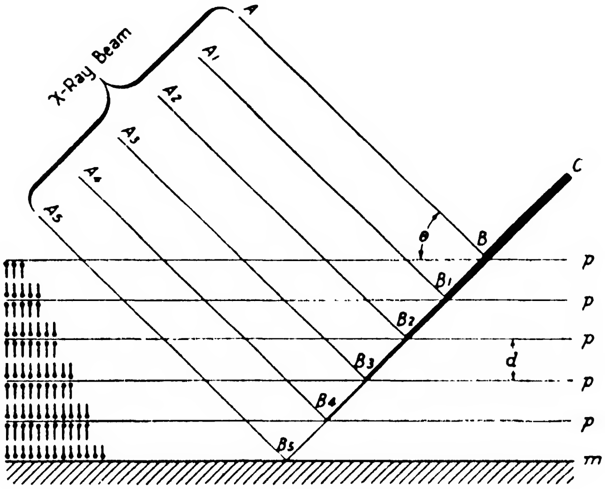


FIG. 2.

The relationship between the factors affecting the diffraction of the X-ray beam are given in the fundamental formula:

$$n\lambda = 2d \sin \theta,$$

in which n represents the number of the order of diffraction, λ the wave-length, d the distance between the diffracting planes, and θ the angle of incidence.

If an X-ray diffraction photograph be taken of a crystal in which the molecules are arranged in a perfectly orderly fashion in all three dimensions, the result is a geometrically arranged series of sharply defined spots of light. The example given in Fig. 3 is the diffraction picture of an iron crystal, and shows the perfect pattern resulting from complete molecular arrangement or regimentation.

On the other hand, if an X-ray photograph be taken of material in which the molecules are of varying sizes and shapes and the arrangement is random, the result is a diffused halo, as shown for a hydrocarbon lubricating oil in Fig. 4. No diffraction lines or spots are to be found, and no orderly molecular arrangement is indicated.

It will be realized that any intermediate stage between perfect molecular regimentation as shown by a crystal (Fig. 3) and complete random arrangement, as in Fig. 4, may be obtained, depending upon the relative degree of molecular arrangement. Fig. 5 is a typical diffraction photograph showing partial orientation. The more complete the molecular arrangement, the shorter and sharper are the arcs. The greater the number of molecular layers in the oriented film, the greater the number of orders of diffraction obtained.

Polar-Film Thickness of Pure Compounds

By our study of X-ray photographs it has been found that a number of oxygen- and chlorine-containing compounds give extraordinarily well-oriented films on metal surfaces. In some cases, as previously shown, the thickness of the layers corresponds to twice the length of the molecules; or, in other words, each building unit consists of a pair of molecules attached end to end, as shown in Fig. 1 c. Table IX shows the thickness of each layer, in Å.U., and the type of arrangement of a number of polar compounds. Referring to methylstearate of single-molecular arrangement and methyldichlorostearate of double-molecular arrangement, we find that the molecular length with the double molecules is not as great as twice the single-molecular length. This reduction in length with double-molecular arrangement is probably due to the mutual saturation of fields of force at the polar ends. Our investigation confirms the conclusions of Adam [1, 1922, 1923, 1930] and Gilson [19, 1928] that oxygen plays a very important part in the formation of these protective polar films.

It is apparent that, knowing both the thickness of each molecular layer and the number of layers required for each diffraction arc, it would be possible to calculate the thickness of the whole adsorbed film. The thickness of the layers is shown in Table IX. It is now possible to determine the number of molecular layers in the adsorbed film which is required to produce a microphotometrically detectable order on the photographic plate.

TABLE IX

Layer Thickness and Molecular Arrangement of Oriented Films

Polar compound	*Layer thickness*	*Molecular arrangement*
Stearic acid	39·5	double
Dichlorostearic acid	39·2	double
Methylstearate	26·5	single
Methyldichlorostearate	45·0	double
Methylpalmitate	22·2	single
Ethyldichlorostearate	51·5	double
Cetyldichloroacetate	27·6	single
Octadecyldichlorostearate	42·9	doubtful

The determination of this factor depends on the technique developed recently by Blodgett and Langmuir [7, 1934, 1935; 27, 1916–17, 1920, 1934] for the application of mono-molecular films one at a time to a solid surface. As reported by Clark, Sterrett, and Leppla [11, 1932, 1935], we used this method to apply known numbers of molecular layers of certain polar materials to various solids. By making X-ray photographs at progressive stages, it was possible to determine the minimum number of layers necessary to produce a microphotometrically detachable order of diffraction on the photographic plate. The minimum for non-metallic polar compounds was found to be from 19 to 45 layers—depending on the type of molecule being adsorbed. For example, Table X shows the result of picking up mono-molecular layers of stearic acid from pure water on a brass rod. It will be observed that, since 71 molecular layers show only the third order and 125 show the fifth order, approximately 25 molecular layers are required for each diffraction order. The relative intensity of the odd orders is, as a rule, greater than the intensity of the even orders, as shown by the table.

TABLE X

Orders of Diffraction of Films of Stearic Acid on Brass

No. of molecular layers	*Relative intensity by order number*				
	1	*2*	*3*	*4*	*5*
71	7	0·5	2·5	0	0
125	12	3·0	4·7	0	1

The product of the minimum number of layers and the number of orders appearing gives the minimum number of molecular layers which must have been formed. Since stearic acid shows seven diffraction orders, each requiring approximately 25 mono-molecular layers or 12½ double layers of 39·5 Å.U. thickness (see Table IX), this film must be approximately 3,500 Å.U. thick. Upon esterifying stearic acid, the polarity is decreased so that only 3 diffraction orders appear. Therefore, assuming the minimum 19 molecular layers for each diffraction arc, the film thickness with the ester would be only 1,500 Å.U. However, on chlorinating the ester, 21 diffraction orders appear. Taking the minimum number of molecular layers required for each order, and assuming that a linear relationship holds for 21 orders, the film thickness of the chlorinated ester is approximately 9,000 Å.U. This figure is of enormous magnitude in the field of molecular dimensions, and is in good agreement with early estimates of Hardy [20, 1918–20, 1922, 1926, 1928] and Trillat [43, 1926–8].

The high orders of diffraction shown by the chlorinated ester are quite interesting, as their appearance indicates an unusually high degree of orientation. From ample data concerning the length of these molecules, we know the arrangement is perpendicular to the metal surface and that the spacings represent the length of the molecules. This fact, coupled with the absence of side spacing, indicates the cross-bonding between the molecules by secondary forces—which stabilizes the oriented molecules. This secondary bonding is obtained, as previously pointed out, by the chlorines on the alpha-carbon atom. The bonding of the polar molecules on the metal surface, and the cross-bonding with the chlorine, is accomplished to such a degree that in some cases X-ray patterns indicate a new condensed molecular arrangement near the metal surface.

Effect of Metal Surface

Polar compounds will not orient to the same degree on different metals. Table XI shows the results obtained using pure compounds on various metals. The numbers in the table have reference to the relative rating of orientation observed for the particular compound on the series of metals. No comparison is made between the various compounds. The number 1 signifies the best orientation;

TABLE XI

Orientation of Polar Compounds on Various Metals

Substance	*Iron*	*Zinc*	*Cadmium*	*Copper*
Stearic acid	..	2	3	1
Methylstearate	2	1	1	..
Octadecylchlorostearate	1	2	2	3
Ethyldichlorostearate	1*	2†	2†	..
Monochlorodiphenylene oxide	1	1	1	2
Trichlorophenol	1	1	3	4
Trichloronaphthalene	1	1	1	1

* Twenty-one orders of diffraction present.
† Fifteen orders.

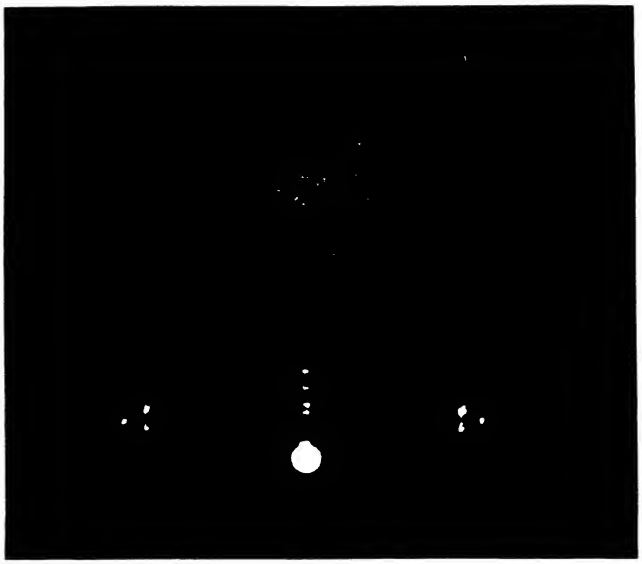


Fig. 6

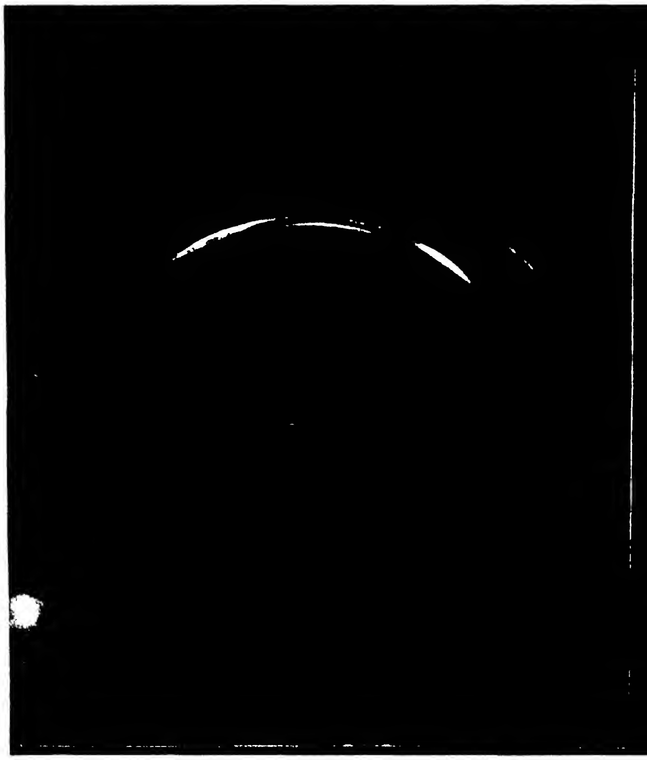


Fig. 8 b

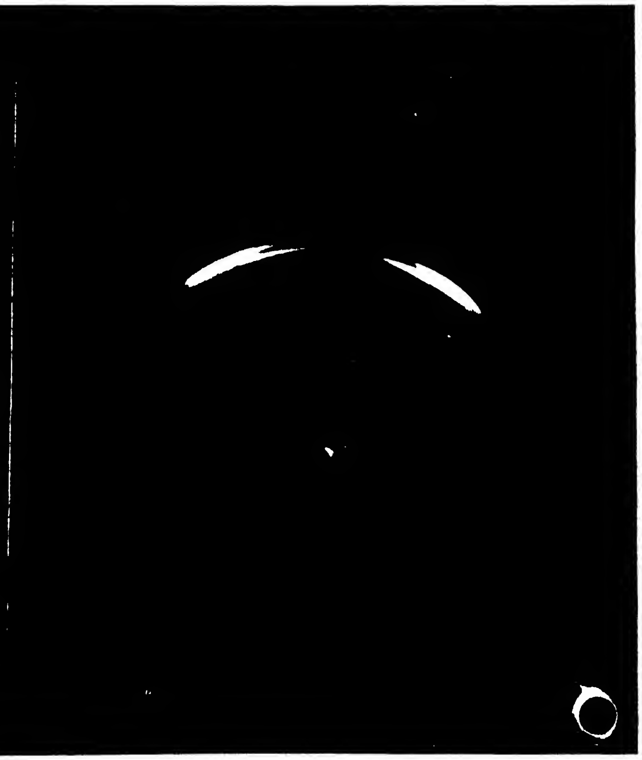


Fig. 8 a

2, the next best, &c. It will be seen that most of the compounds form their thickest film on iron, and that the chlorinated ester forms extremely thick films on all the metals except copper, as proved by the unusually large number of orders of diffraction shown for ethyldichlorostearate.

In addition to determining the minimum thickness of polar films on metal surfaces, we have determined by study of mono-molecular layers the actual metal-surface area occupied by each polar molecule. Molecules such as methyldichlorostearate cluster together side by side on the metal surface, and are separated by the thickness of the molecule only. The area covered by each of these molecules, with maximum spreading on a surface, has been found to be 20 sq. Å.U.

Orientation in Solution

We find that polar compounds in dilute hydrocarbon-oil solution, such as is used in practical lubrication, orient on metal surfaces more or less completely as they do in the pure state.

It is not possible to see the total number of orders of diffraction in the case of X-ray photographs of solutions of polar addition agents in mineral lubricating oil, because the diffused halo due to the mineral oil completely masks the outer orders or arcs. We have, however, been able to detect as many as seven distinct orders inside the oil halo when using a dilute solution of chlorinated ester. It is, therefore, evident that bearing surfaces are separated by more than 6,000 Å.U. when a chlorinated ester is used in a lubricating oil. Thus, this oriented film is approximately as thick as the previously proved minimum film thickness for viscous lubrication.

Regimentation in Solution

The polar molecules in dilute solution not only orient upon the metal surface to a degree approaching perfection, but also arrange themselves in an orderly fashion throughout the mass of the liquid and tend to direct the regimentation of the molecules of the hydrocarbon lubricant. Similar cybotactic regimentation has been amply substantiated by Stewart [39, 1929, 1930, 1933, 1934] and by many others [4, 1930; 11, 1932, 1935; 25, 1928; 36, 1928].

This characteristic was investigated by studying the effect of the presence of polar compounds upon the crystallization of paraffin wax from oil-wax solution. Wax crystallizes in a randomly arranged mass of small crystals, giving a partially oriented diffraction picture in many respects similar to Fig. 5. When 5% of a highly polar compound such as methyldichlorostearate is added to the wax-oil solution, the resultant diffraction pattern is given in Fig. 6. The intense short arcs, on both the vertical and horizontal axes, represent substantially perfect orientation and regimentation. The broad diffused oil halos, representing the side spacings of the molecules, have been replaced with short, sharply defined spots on the horizontal axis. As far as we know, this is the first completely regimented arrangement reported for the molecules in a hydrocarbon mixture. The polar compounds arrange themselves in a widely-spaced lattice structure, which might be likened to the structure in a honeycomb. This orderly regimentation is such that, when the wax crystallizes from the solution, the lattice structure is impressed upon the wax crystals—which grow or arrange themselves in conformity with the regimentation of the polar molecules.

Regimentation in Lubricating Oil

The effect of polar compounds upon molecular regimentation in lubricating-oil solutions is not as easily demonstrated as in the case of the wax solutions. The X-ray photograph of a lubricating oil (Fig. 4) gives no visible indication of oriented molecular layers. However, the pattern may be investigated by microphotometric analysis, thereby showing the variations of the intensity of the diffracted X-ray beam radially through the oil halo. These variations in the intensity of the halo will be found dependent upon the degree of cybotactic arrangement. Increasing temperature tends to destroy regimentation and produce a more chaotic molecular arrangement. Therefore if a microphotometer analysis be made at several increasing temperatures, it will be found that the maximum variation in intensity becomes less and the halo broadens and becomes more diffused.

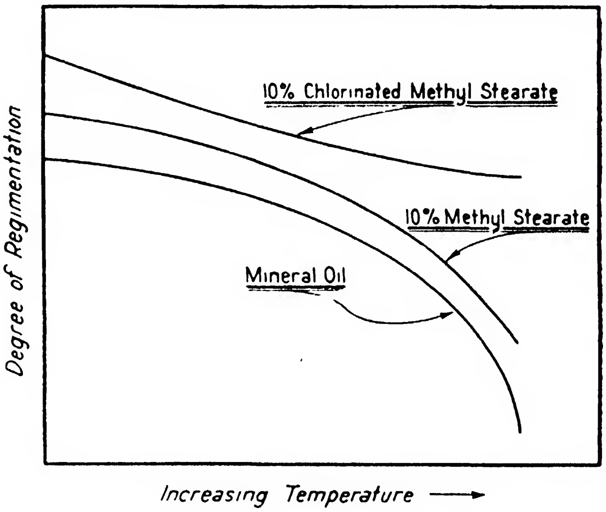


FIG. 7.

This method, therefore, permits the investigation of the effect of polar molecules in the oil, since the regimentation of a polar compound would tend to resist the disorganizing effect of increased temperature. Fig. 7 illustrates the effect of the presence of 10% of methylstearate and of methyldichlorostearate on the temperature-regimentation curve. The slopes of the curves show the relative decrease of regimentation with increasing temperatures. The vertical position of the curves is not significant, as the sensitivity of the microphotometer was not the same. From the figure it will be noted that the curves for mineral oil and methylstearate slope downward, showing marked decreases in the degree of regimentation with increasing temperature. The curve for the blend of oil and methyldichlorostearate shows a very small decrease in degree of regimentation, with the curve flattening out at the higher temperatures. This study was conducted through a temperature range up to approximately 250° C. Further investigations by this method disclosed that the amount of regimentation is directly proportional to the concentration of the methyldichlorostearate.

We may conclude from these examinations that molecules of chlorinated esters are highly regimented in the liquid state by their strong bonding force. These bonding forces of the polar molecules affect the oil molecules by reducing their tendency towards more random arrangements with temperature increases.

Metal-fibre Protection as a Measure of Lubricating Ability

Many types of laboratory and field tests have been employed to prove that a film of the polar compound is beneficial in lubrication. By X-ray technique we have found that certain polar compounds in a lubricant will protect rubbing surfaces. Our experiments were based on the crystalline arrangement at the surface of worked metals.

In forming metals into desired shapes by drawing, stresses are applied which serve to arrange the surface metallic crystals with a preferred orientation which may be termed 'fibering', because of the resemblance of the X-ray pictures of these surfaces to those of natural fibres. If a metal showing such 'fibering' is re-worked so that the direction of stress is at right angles to the original stress, the first set of fibres will tend to disappear. The macroscopic directional striations, sometimes visible on the surface of metals due to working, are not susceptible to X-ray examinations as are the effects due to crystalline arrangement.

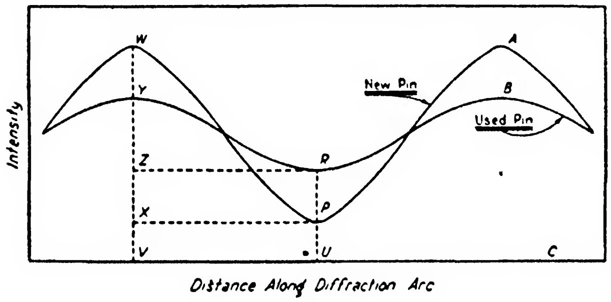


FIG. 9.

The changes in crystal structure due to working were utilized in determining the value of polar compounds in lubricants for protecting metal surfaces and preventing wear and, hence, their lubricating value. A drawn brass rod, showing suitable 'fibering' in a direction parallel to its axis, was made into Almen pins. After X-ray photographs had been made of these pins to measure the degree of original crystal orientation, they were run for five minutes in the Almen machine with various lubricants, using a load of 2,000 lb. per sq. in. of projected bearing area and a speed of 600 r.p.m. This load was selected because it is not great enough to destroy completely the surface fibre structure during the test period when a satisfactory polar compound is included in the lubricant. Photographs of the pin surfaces, after the test, were made and compared with the first photographs.

Fig. 8 A shows a typical picture of the fibre structure before use, while Fig. 8 B gives the result on the same pin after use. In Fig. 8 A the difference in intensity of the metal-diffraction lines between the maximum and minimum points is readily seen, while in Fig. 8 B it will be noticed that the variation in intensity is much less. While the differences in intensity of different parts of a metal halo are apparent to the eye in cases such as are represented in Fig. 8 A and 8 B, they are more often sufficiently difficult to discern so that advantage must be taken of a microphotometer to discover these variations in intensity. By measuring in this way the intensity of the light at various points along a halo, one may plot intensity against distance —obtaining curves such as shown in Fig. 9.

Curve *WPA* represents the intensities around one semicircular line of the X-ray pattern of the new Almen pin (see Fig. 8 A) and curve *YRB* shows the same for the used Almen pin (see Fig. 8 B). The peak height of the curves compared with an adjacent point of minimum intensity is directly proportional to the number of metal crystals having that particular orientation.

Hence $\frac{YZ}{WX} \times 100$ gives the percentage of fibred structure remaining on the surface of the metal after the test.

TABLE XII

Metal-surface Protection by Blended Lubricants

	Unit load (lb. per sq. in.)	*Fibre remaining %*	*Timken film strength (lb.)*
Oil with 1% of:			
Mineral oil . . .	2,000	0	8·8
,, ...	1,000	0	..
Dichlorostearic acid . .	2.000	37	38·5
Methyldichlorostearate .	2,000	47	28·0
Chlorodiphenylene oxide .	2,000	40	28·0
Chlorodiphenyl . . .	2,000	0	25·5

In this way the data on the various blends shown in Table XII were obtained. It is apparent from the table that, using a straight mineral oil and a load of only 1,000 lb. per sq. in., the 'fibering' was completely destroyed. Additions of 1% methyldichlorostearate to the mineral oil gave excellent protection of the surface, as shown by the fact that after the test 47% of the original surface 'fibering' remained unchanged at twice the load.

Summary

The physico-chemical forces emanating from metal surfaces and from certain types of molecules, known as polar molecules, profoundly affect the behaviour of the metals and lubricants involved in boundary lubrication, and are of importance in viscous lubrication. The attractive forces between metal surfaces bearing one on another are neutralized by strongly polar molecules, such as chlorinated esters of long-chain fatty acids and short-chain monohydric alcohols, so that lubrication is improved. This is accomplished by the formation of a film in which the polar molecules are firmly bound in an orderly fashion with respect to each other and to the metal surface.

Evidence of the action of these forces has been found in various physical measurements which serve as preliminary indications of the adsorption of polar molecules to form oriented films, but this investigation was directed to the fundamental study of the physical and chemical forces involved and the films formed.

Under conditions of viscous lubrication, dilute mineral-oil solutions of highly polar compounds, such as methyldichlorostearate, neutralize the fields of force emanating from metal surfaces by forming an oriented film and by regimenting hydrocarbon molecules in the liquid body of the lubricant which affords slippage planes of minimum resistance. These actions of the polar films are of importance in explaining the anomalous coefficients of friction in viscous lubrication. X-ray investigation of adsorbed film structures of pure compounds shows that the type of molecular building unit, regularity of arrangement, and the number of molecular layers formed depend on the compound and on the metal. The strongly polar molecules of certain chlorinated esters form adsorbed films on metals of unusual thickness and regularity of arrangement. The thicknesses of these oriented films of strongly polar compounds on metal surfaces are of enormous magnitude when compared to molecular dimensions. The present results show a film thickness of 9,000 Å.U., which serves as a confirmation of Hardy's measurement of 10,000 Å.U., Trillat's of 9,000 Å.U., and Tausz's of 8,500 Å.U.

In order to demonstrate that the orienting ability of the pure polar compounds is also effective in dilute solution, oil-wax mixtures were investigated. In dilute mineral-oil solution, methyldichlorostearate forms films of such thickness that a pair of metal surfaces approaching the limit of viscous lubrication of about 6,000 Å.U. are separated by a completely oriented film of polar molecules.

The stability of the regimented (cybotactic) groups of polar addition agents in lubricating-oil solution is demonstrated by the resistance of methyldichlorostearate blends to the disorganizing effect of temperature increases.

By means of a new method of measuring changes in the surface structure (fibering) of metals, it has been shown that lubricants containing methyldichlorostearate actually protect rubbing metal surfaces from wear.

Acknowledgment

The authors wish to acknowledge the assistance of W. L. Steiner and G. D. Byrkit, of the research staff of Continental Oil Company, in the execution of this work and in the preparation of this paper.

APPENDIX

During the preparation and publication of the present article more detailed studies of some of the subjects discussed here have appeared. The use of the Timken machine for the preliminary investigation of the behaviour of a wide variety of halogen compounds has been described by Bert H. Lincoln, Gordon D. Byrkit, and Waldo L. Steiner (*Ind. Eng. Chem.* **28**, 1191 (1936)). By carefully controlling the conditions of the Timken test and by expressing the results in terms of the Timken index, differences in the structure of the organic molecules are rendered comparable. Generalizations are presented, attempting to correlate the structure of the addition agent with its effect on Timken film strength.

The experimental methods used in the X-ray investigations are described in considerably greater detail by George L. Clark, Robert R. Sterrett, and Bert H. Lincoln (*Ind. Eng. Chem.* **28**, 1318 (1936)) in three articles covering the structures of solid and unimolecular films, orientation effects of additional agents, molecular regimentation and chemical reactions in liquid oils and blends and the X-ray method of rating lubricants in terms of protection against surface wear.

REFERENCES

1. Adam, N. K. *Proc. Roy. Soc. Gt. Brit.* **101** A, 452 (1922); **103** A, 676 (1923); *Physics and Chemistry of Surfaces* (Oxford University Press, 1930).
2. Allen, H. S. *Proc. Phys. Soc.* **32**, 165 (1919).
3. Bachmann, W., and Brieger, C. *Kolloid-Z.* **36** A, 142 (1925).
4. Banerjee, K. *Indian J. Physics*, **4**, 541 (1930).
5. Barnard, D. P., and Forrest. *Ind. Eng. Chem.* **16**, 327 (1920).
6. Becker, A. E. *Ind. Eng. Chem.* **18**, 471 (1926).
7. Blodgett, K. B. *J.A.C.S.* **56**, 495 (1934); **57**, 1007 (1935).
8. Blom, I. J. *Petr. Z.* **25** **(46)**, Suppl. 3, Nov. 13 (1929).
9. Bragg. *Nature*, **115**, 266 (1925).
10. Bridgeman, P. W. *Physics*, **5**, 125 (1934).
11. Clark, G. L., *et al.* *J.A.C.S.* **57**, 330 (1935); *Applied X-Rays*, 2nd ed. (New York 1932).
12. Dallwitz-Wegner, R. *Kolloid-Z.* **38**, 193 (1926).
13. Deeley, R. M. *Proc. Phys. Soc.* (*London*) (2), **32**, 1-s (1920); *Engineer*, **131**, 78 (1921).
14. Department of Scientific and Industrial Research (England), Technical Papers 1 (1930) and 2 (1934).
15. Devaux. *J. phys.* (4), **3**, 450 (1904); (5) **2**, 699, 891 (1912).
16. Dunstan, A. E., and Thole, F. B. *J.I.P.T.* **4**, 191 (1918); *Chem. and Met. Eng.* **28**, 299 (1923).
17. Ewing. *Proc. Royal Inst. Gt. Brit.* **13**, 387 (1892).
18. Gill. *Mech. Eng.* **57**, 413 (1935).
19. Gilson, E. G. *Ind. Eng. Chem.* **20**, 847 (1928).
20. Hardy, W. B. *Kolloid-Z.* **46**, 268 (1918); *Phil. Mag.* (6), **38**, 32 (1919); **40**, 201 (1920); *Proc. Royal Soc. Gt. Brit.* **100** A, 181, 550 (1922); **112** A, 62 (1926); **118** A, 209 (1928).
21. Herschel, W. H. *Bull. 112, Amer. Instrument Co.* (1929); *Chem. and Met. Eng.* **28**, 302 (1923).
22. Hersey. *J. Wash. Acad. Sci.* **23**, 297 (1933); *Mech. Eng.* **55**, 561 (1933).
23. Kadmer. *Oel und Kohle*, **11**, 116 (1935).
24. Karplus, H. *Petr. Z.* **25**, 375 (1929).
25. Katz, J. R. *Z. angew. Chem.* **41**, 329 (1928).
26. Kingsbury. *Trans. Amer. Soc. Mech. Engrs.* **24**, 143 (1903).
27. Langmuir, I. *J.A.C.S.* **38**, 2221 (1916); **39**, 1848 (1917); *Trans. Faraday Soc.* **15**, 62 (1920); *J. Franklin Inst.* **218**, 143 (1934).
28. Lincoln, B. H., *et al.* U.S.P. 1,936,670; 1,939,979; 1,939,993; 1,939,994; 1,939,995; 1,944,941; 1,945,614; 1,945,615; 1,959,054. B.P. 422,956 (1935). F.P. 761, 243 (1935). Italy P. 326,175. Argentina P. 42,066 (1934). Australia P. 13,923 (1933). Brazil P. 22,062 (1934). Cuba P. 10,441 (1934). Mexico Pats. 36,052; 35,867; 35,663; 34,404.
29. Lubricant and Lubrication Inquiry, Committee, Department of Scientific and Industrial Research (England) (1920).
30. Marcelin. *Ann. phys.* (9), **1**, 19.
31. Meyer, K. H. *Z. angew. Chem.* **41**, 935 (1928).
32. Mueller, A., and Shearer, G. *J.C.S.* **123**, 3156 (1923).
33. Murison. *Phil. Mag.* **17**, 201 (1934).
34. Parrish and Cammen, preprint. Amer. Soc. Mech. Eng. meeting, June (1932).
35. Parsons, L. W., and Taylor, G. R. *Ind. Eng. Chem.* **18**, 493 (1926).
36. Prevost, C. *Rev. gén. sci.* **39**, 663 (1928).
37. Rayleigh. *Phil. Mag.* (6), **35**, 157 (1918).
38. Stanton. *Engineer*, **135**, 678 (1923).
39. Stewart. *Chem. Reviews*, **6**, 483 (1929); *Rev. Modern Phys.* **2**, 116 (1930); *Indian J. Physics*, **7**, 603 (1933); *Kolloid-Z.* **67**, 130 (1934).
40. Sub-committee on Lubrication. *Mech. Eng.* **41**, 537 (1919).
41. Tausz, J., *et al.* *Z. angew. Chem.* **43**, 570 (1930); *Erdöl und Teer*, **9**, 331 (1933).
42. Tomlinson, G. A. *Phil. Mag.* (7) **7**, 904 (1929).
43. Trillat, J. J. *Rev. sci.* **64**, 552 (1926); *Ann. phys.* **10**, 5 (1926); *Compt. rend.* **182**, 843 (1926); **187**, 168 (1928); *Mech. Eng.* **50**, 471 (1928); *Metallwirtschaft*, **7**, 101 (1928); *Halle aux cuirs, Suppl. tech.* 137 (1927).
44. Wells, H. M., and Southcombe, J. E. *J.S.C.I.* **39**, 51 T (1920).
45. Wilharm, W. C. *Ind. Eng. Chem.* **18**, 463 (1926).
46. Wilson, R. E., and Barnard, D. P. *Ind. Eng. Chem.* **14**, 682 (1922). *S.A.E.J.* **11**, 49, 143 (1922).
47. Wolf, H. C., and Mougey, H. R. *Proc. A.P.I.* **13**, (iii), 118–31 (1932).
48. Woog, P. *Compt. rend.* **180** (1924); **181**, 772 (1925); **186**, 71 (1928); *L'Étude du Graissage*, Paris (1926).

THE CHEMICAL NATURE OF LUBRICATING OILS

By F. B. THOLE, D.Sc., F.I.C.

Chemist, Anglo-Iranian Oil Company, Ltd.

ALTHOUGH a considerable number of somewhat unsystematic and sporadic attempts have been made to elucidate the problem of the chemical nature of the hydrocarbons in lubricating oil, the amount of reliable information on this subject is strikingly small. This is perhaps hardly to be wondered at when one considers the difficulty involved in an analytical study of a mixture of many hydrocarbons which may include not only paraffins, naphthenes, aromatics, and olefines, but molecular structures in which paraffin-naphthene, naphthene-aromatic, or paraffin-aromatic-olefine systems may be linked together.

That all or most of these groupings are present is shown by the facts that:

(*a*) Analysis indicates an empirical formula generally lying between C_nH_{2n} and C_nH_{2n-8}, the C/H ratio being least in the so-called (and probably mis-called) paraffin or Pennsylvanian type and greatest in the so-called asphalt-base oils.

(*b*) The oils generally show a small iodine value ranging from nearly zero up to 10. This value is never precise as in the case of most fatty oils but depends considerably on the experimental details of the method used [5, 1916], and this difference from the rapid and definite iodine (or bromine) absorption characteristic of olefinic compounds has led many chemists to doubt if olefinic systems are present in the oil unless (as is not usually the case) deliberate cracking has been employed in the distillation process.

(*c*) Aromatic ring systems are indicated by the fact that many of these oils give solid products with formaldehyde and sulphuric acid (the 'formalite reaction') and will moreover absorb hydrogen in the presence of catalytic nickel with consequent creation of naphthene rings.

Normal paraffins (which at this molecular weight viz. 400–500, are high-melting solids) must be absent, but possibily branched chain paraffins are present. Many of the more complex aromatic ring compounds derived by hydrogenation of phenanthrene, chrysene, retene, and picene, as well as numerous alkylated derivatives of diphenyl, have been synthesized and some of these are liquids with a viscosity, boiling-point, and molecular weight not dissimilar from those of lubricating oil fractions, but there is no evidence of their presence in the natural material. It is probable that the fluorescent colouring matter in most unrefined lubricating oils is aromatic in structure, a probability confirmed by the fact that it is extracted by concentrated sulphuric acid and is destroyed by hydrogenation, but the amount in any case is almost infinitesimal.

By extraction with selective solvents such as SO_2, phenol, furfural, or nitrobenzene, petroleum lubricating oils may be separated into fractions of greater and lesser solubility in the solvent used. The more soluble fraction, in which no doubt the aromatic and olefinic molecules, if present, are concentrated, has the higher C/H ratio, the greater degree of unsaturation towards hydrogen, the greater tendency to oxidation to asphaltic matter, and the lower viscosity index, and in these respects such an 'extract' is not dissimilar from the complex hydrocarbons obtained by polymerizing ethylene and other simple olefines by heat or by catalysts nor from the products obtained by condensing aromatic hydrocarbons with olefines or with chlorinated paraffins. This fraction is, however, regarded as undesirable in a refined lubricating oil and is eliminated in the process of refining.

While it is very evident that precise information as to the hydrocarbons in lubricating oil is almost non-existent, no hydrocarbon of known constitution ever having been isolated from or identified in a lubricating oil, some knowledge of the structures present can be obtained by the methods recently developed by Vlugter, Waterman, and van Westen [6, 1932, 1935]. According to these investigators the molecular complexity of these hydrocarbons is such that their structure can best be expressed in terms of percentage aromatic rings, percentage naphthenic rings, and percentage paraffinic chains. To illustrate the proposal one may consider ethyltetrahydronaphthalene which is a molecule containing an aromatic ring, a naphthene ring, and a paraffinic side-chain. The formula $C_6H_4.C_4H_7.C_2H_5$ is thus equivalent to 48% (by weight) of aromatic rings, 34% naphthenic rings, and 18% paraffinic chains.

By determining the mean molecular weight of a lubricating oil fraction and the amount of hydrogen it will absorb on hydrogenation with a nickel-kieselguhr catalyst the percentage of aromatic nucleus can be determined. By then determining the specific refraction of the hydrogenated product the proportion of naphthene rings to paraffinoid chains can be calculated from curves previously prepared from data derived from the refractivity-molecular weight relationships of known paraffins and simple and polynuclear naphthenes. It becomes possible in this way to state that a certain Pennsylvanian oil fraction with a mean molecular weight of 512 consists of 8% aromatic rings, 15% naphthenic rings, and 77% paraffinic chains, while a certain 'naphthene base' oil of mean molecular weight 349 contains 32% of aromatic rings, 29% of naphthene rings, and 39% paraffinic chains. It is, of course, not possible to decide if the paraffinic chains are side-chains attached to aromatic or naphthene rings or whether they are separate purely paraffinoid hydrocarbons, though the low melting-point precludes the presence of normal paraffins. Nevertheless this method of attacking the problem is the only one yet devised which has afforded any insight into the chemical nature of the hydrocarbon structures present in these oils.

Mikeska [4, 1936], realizing the practical impossibility of recognizing by analytical methods any individual hydrocarbon in a lubricating oil, prepared a large number of synthetic hydrocarbons consisting of various combinations of aromatic and hydroaromatic nuclei with each other and with short and long side chains. The chief physical properties of these, such as viscosity-temperature relationship, optical properties, aniline point, and specific gravity, were then tabulated and form a sounder basis than most of the previously recorded data for deductions as to the chemical constitution of hydrocarbons of high molecular weight. Mikeska's paper contains a detailed bibliography of earlier (and often erroneous) publications on this subject. Another worker on similar 'synthetic' lines is Hugel [1, 1931] who prepared a series of aromatic, hydro-aromatic, and paraffin hydrocarbons and recorded some of their physical properties.

With information thus available Mair and Willingham [3, 1936] at the Bureau of Standards approached the problem from the analytical side. They took as starting material an Oklahoma lubricating oil and by extraction with sulphur dioxide, filtration through silica gel, and dewaxing prepared a stock of a water-white hydrocarbon mixture. This was separated by systematic fractional distillation in vacuo into a series of sharply cut fractions of close boiling range. Each fraction was then fractionally extracted with acetone and thus divided into some thirty sub-fractions. They then determined the empirical formula, molecular weight, and many physical properties of a selection of these fractions and compared the data with those of Mikeska's synthetic hydrocarbons of known constitution. Where there is a close resemblance in many properties between a fraction and a synthetic hydrocarbon of known constitution it is a reasonable assumption that a structural similarity exists. The conclusions arrived at are that the least soluble fractions, i.e., those corresponding with a highly refined (solvent extracted) lubricating oil consist substantially of naphthenes containing from one to three rings in the molecule with attached alkyl groups. The more soluble portions consist of naphthenes with more than three rings together with some unsaturated hydrocarbons and possibly some aromatics. There is no evidence for the presence of iso- or branched chain paraffins. It is not improbable that the most soluble fractions contain both one-ring aromatics and multi-ring (approximately six-ring) naphthenes.

It will be noted that these conclusions, which seem the soundest yet available, support the views of Vlugter, Waterman, and van Westen and not those of Kyropoulos [2, 1928] who from a study of density-refractivity relationships concluded that iso-paraffins were present in considerable quantities. It is noteworthy that all analyses on record of lubricating oils show a negative value for x in the formula $C_n H_{2n} + x$, though, of course, a mixture of iso-paraffins and dicyclic naphthenes would still give a mean formula with x as a negative quantity.

In addition to hydrocarbons all petroleum lubricating oils contain small proportions of sulphur compounds and possibly also oxygen compounds. These, like the more reactive hydrocarbons, are to a considerable degree removed by sulphuric acid treatment or by extraction with selective solvents in the course of refining, but very drastic extraction with sulphuric acid is necessary to effect approximately complete elimination. The normal sulphur content of a refined lubricating oil generally lies between 0·2 and 1·5%, which on a basis of a mean molecular weight of 450 would imply a content of sulphur compounds between 3 and 20%. We have no knowledge, however, as to the molecular weights of such sulphur compounds nor as to which classes of sulphur compounds (mercaptans, sulphides, disulphides, or sulphur-ring structures of the thiophen or thiophane type) are present. Whatever their type, however, they are very stable for a well-refined lubricating oil even with a sulphur content approaching 2% has to be inert to copper and other metals with which it is in contact when in use.

As regards oxygen compounds, again practically nothing is known, but most oils, especially the highest-boiling fractions, show a small saponification value, generally below 1, which implies the presence of traces of esters or lactones.

Since nitrogen compounds (mainly quinoline derivatives) are known to be present in small amounts in the kerosine and gas-oil fractions of certain petroleums (notably in California) it is probable that they are also present in unrefined lubricating oil. As, however, sulphuric acid is generally employed in some stage of the refining process it is highly improbable that any of these bases will be present in the refined oil and none has been recorded.

REFERENCES

1. Hugel, G. *Chim. et Ind.* **26**, 1282 (1931).
2. Kyropoulos, S. *Z. physik Chem.* **144** A, 22–48 (1928).
3. Mair, B. J., and Schicktanz, S. T. *Ind. Eng. Chem.* **28**, 1446–1460 (1936).
4. Mikeska, L. A. *Ind. Eng. Chem.* **28**, 987–983 (1936).
5. Radcliffe, L. G., and Polychronis, C. *J.S.C.I.* 340 (1916).
6. Vlugter, J. C., Waterman, H. I., and van Westen, H. A. *J.I.P.T.* **18**, 735 (1932); **21**, 66 (1935).

DENSITY, REFRACTIVE INDEX, AND RELATED CHARACTERISTICS OF LUBRICATING OILS AND BITUMINOUS SUBSTANCES

By A. L. WARD, *Manager, Chemical Laboratories, The United Gas Improvement Company*; S. S. KURTZ, Jr., *Development Engineer, The Sun Oil Company*; W. H. FULWEILER, *Consulting Chemical Engineer*

(*a*) Gravity in the Examination and Classification of Lubricating Oil.

Lubricating oils may be divided into three general classes: (1) paraffinic oils, (2) mixed base oils, and (3) naphthenic oils.

The paraffinic-type oils change viscosity less rapidly with temperature than the naphthene base oils. The naphthene base oils show less carbon deposit in the Conradson carbon test [2, 1930] than paraffinic oils. Although there is little real experimental evidence for the superiority of paraffin base oils in actual service, oils of this type are at present favoured by many large producers. There has, therefore, been much interest in the use of physical constants to distinguish between oils of these various classes.

At present the situation is further complicated by the appearance on the market of hydrogenated oils, oils which owe their good viscosity slope to the addition of small proportions of compounds of colloidal dimensions and of approximately straight-chain type, and also by the production of oils prepared by solvent extraction.

For a given boiling-point (or viscosity) low density (high API. gravity) has long been recognized as an indication of paraffinic quality. Table III (*vide infra*) shows the increase in density on passing from paraffinic-type to naphthenic-type lubricating cuts. These data were interpolated from enlarged reproductions of the curves of Hill and Ferris [8, 1925]. On the basis of data of this type Hill and Coats [7, 1928] developed the viscosity-gravity constant which may be very conveniently used for classifying lubricating oils.

This constant is given by the equation

$$a = \frac{10G - 1\cdot0752\log(V_1 - 38)}{10 - \log(V_1 - 38)},$$

where G = sp. gr. 60°/60° F. (15·56° C.) and V_1 = Saybolt Universal viscosity at 100° F. (37·8° C.); or

$$a = \frac{G - 0\cdot24 - 0\cdot022\log(V_2 - 35\cdot5)}{0\cdot755},$$

where V_2 = Saybolt Universal viscosity at 210° F.

An alinement chart for calculating this constant is given in the Appendix [9, 1931]. A formula based on kinematic viscosity for use with low-viscosity oils will be found in the section on Diesel Fuels. All the lubricating cuts of a normal crude have, as a general rule, and with few exceptions, the same viscosity-gravity constant. This constant is not a function of boiling-point or molecular weight. Some crudes, however, particularly naphthenic crudes, have a large variation in viscosity-gravity constant, as shown in Fig. 1 for typical Gulf Coast oils labelled no. 2 and Mirando respectively.

McCluer and Fenske [16, 1932] have presented an interesting discussion on the relation between viscosity-gravity constant and viscosity index and have developed a constant of their own called the 'Gravity Index'. The 'gravity index' is determined from the specific gravity at 60° F. and the Saybolt Universal viscosity at 100° F. The 'gravity index' was developed in such a manner that a linear proportionality exists between it and the viscosity index of Dean and Davis. The relations discussed in this article are helpful if it is necessary to predict viscosity slope on the basis of the gravity and the viscosity at one temperature only. As pointed out by McCluer and Fenske, the relations between the various constants are not entirely reliable. For example, the usual relation between viscosity-gravity constant and viscosity index breaks down entirely in the case of synthetic oils prepared by the polymerization of olefines. The writers have also found that the usual relation between viscosity-gravity constant and viscosity index is of no value in the case of blended oils containing hydrogenated rubber or other substances having a beneficial effect on viscosity slope. The change in viscosity-gravity constant in such blends is proportional to the amount of blending agent added, as is the specific viscosity

$$\left(\text{specific viscosity} = \frac{\text{kinematic viscosity blend}}{\text{kinematic viscosity stock}} - 1\right),$$

whereas the change in viscosity index is greatest with the first increment of blending agent. The viscosity index is very generally used, not because it is fundamentally sound, but because there is no general agreement with regard to any better classification. The viscosity-gravity constant is not a substitute for the viscosity index, but it is a valuable constant for classification and one which is related in a simple manner to other fundamental constants.

In Table I viscosity-gravity constants are given for a few representative American crudes. Table II gives the

TABLE I

Viscosity-gravity Constants of the Lubricating-oil Fraction of a few Representative Crudes

Type	*Crude*	*Viscosity-gravity constant*	*Representative value*
Naphthenic	Sourlake, Texas	0·916	0·880
	Miranda, Texas	0·903	
	Heavy Mexican	0·894	
	Sunset, California	0·885	
	Gulf Coast no. 2	0·885	
	Spindle Top, Texas	0·876	
	Gulf Coast no. 1	0·864	
	Light Mexican	0·860	
	Van Zandt County, Texas	0·852	
Intermediate or mixed base (Mid-Continent)	Seminole, Okla.	0·844	0·835
	Reagan County, Texas	0·839	
	Mid-Continent	0·837	
	Salt Creek, Wyo.	0·829	
	Burbank, Okla.	0·828	
	Ranger, Texas	0·827	
Paraffinic	Pennsylvania	0·807	0·805
	Eureka, Pa.	0·804	
	Buckeye, Ohio	0·800	
	Mill Town, Pa.	0·800	

TABLE II

Gravities of Lubricating Oils corresponding to Viscosity Classification of the Society of Automotive Engineers [19, 1932]

Description	*S.A.E. no.*	*Approximate range of Saybolt Universal viscosity*		*Gravity* of S.A.E. oils if prepared from typical crudes having viscosity-gravity constants as follows:*					
				0·805 Pennsylvania		*0·835 Mid-Continent*		*0·880 Gulf Coast*	
		130° F.†	*210° F.*†	*Sp. gr. 60°/60° F.*	*°API. 60° F.*	*Sp. gr. 60°/60° F.*	*°API. 60° F.*	*Sp. gr. 60°/60° F.*	*°API. 60° F.*
Light motor oil	20	120 to 185	(50) to (60)	0·873 0·878	30·7 29·7	0·896 0·901	26·5 25·6	0·930 0·935	20·8 19·9
Medium motor oil	30	185 to 255	(60) to (69)	0·878 0·881	29·7 29·1	0·901 0·904	25·6 25·0	0·935 0·838	19·9 19·4
Heavy motor oil	40	255	(69) to 75	0·881 0·883	29·1 28·8	0·904 0·906	25·0 24·7	0·838 0·939	19·4 19·2
Extra-heavy motor oils	50	..	75 to 105	0·883 0·888	28·8 27·8	0·906 0·911	24·7 23·8	0·939 0·945	19·2 18·2
Extra-heavy motor oils	60	..	105 to 125	0·888 0·891	27·8 27·3	0·911 0·914	23·8 23·4	0·945 0·947	18·2 17·8
Tractor and transmission oils	70	..	125 to 150	0·891 0·893	27·3 26 9	0 914 0·916	23·4 22·9	0·947 0·950	17·8 17·4

* Calculations on basis of viscosity at 210° F. using nomographic chart [9, 1931].

† S.A.E. 50 to 70 oils are specified by viscosity at 210° F.; S.A.E. 20 to 40 are specified on basis of viscosities at 130° F. The 210° F. viscosities on the 20 to 40 S.A.E. oils are only approximate.

ranges of specific gravity which correspond to the viscosity limits for the grades of lubricating oils specified by the Society of Automotive Engineers [19, 1932], assuming that these oils are prepared in turn from lubricating stocks of 0·805, 0·835, and 0·880 viscosity-gravity constant respectively.

(*b*) Specific Gravity, Boiling-point, and Viscosity-gravity Constant.

Specific gravity (60°/60° F.) and viscosity-gravity constant are proportional to each other, for materials of the same boiling-point, as shown in Fig. 1. This figure was constructed from the data of Hill and Ferris [8, 1925] by interpolation. Kurtz [12, 1935] pointed out that a similar linear relation exists between specific gravity and viscosity-gravity constant for the raffinates and extracts from a given stock. For example, using the data of Ferris, Birkheimer, and Henderson [6, 1931] for Stock no. 2, the following equation may be written:

$$\text{v.g.c.} = 1{\cdot}14 \times \text{sp. gr.} - 0{\cdot}185.$$

This equation represents the data for extraction of Stock no. 2 with each of 25 different solvents, at temperatures ranging from −7° C. for sulphur dioxide to 125° C. for furfural. The constancy of the relation is based upon the fact that these solvents separate upon the basis of hydrocarbon type, and that the stock, extract, and raffinate all have approximately the same molecular weight and boiling range. The slope of these lines varies within the range 1·06 and 1·16. For example, the data of Davis and McAllister [4, 1930] show a slope close to 1·10.

This graphic treatment of the boiling-point gravity relation supplements the algebraic treatment of Hill and Coates [7, 1928] and of Jackson [11, 1935]. Fig. 1, for example, may be used in planning the processing of a given stock. Suppose that a lubricating stock of 0·850 v.g.c. is available and that it is desired to produce a lubricating oil of 0·810 v.g.c. having a viscosity of 50 sec. Saybolt Universal at 210° F. From the viscosity-gravity nomograph, one can determine that this oil must have a sp. gr. (60°/60° F.) of

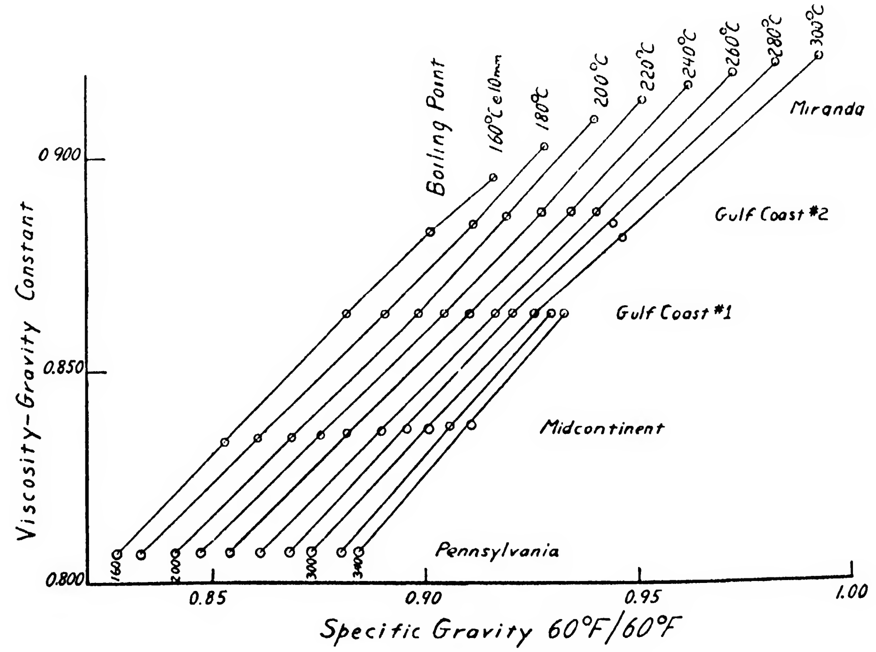


FIG. 1.

0·877. By reference to Fig. 1 it can be seen that to produce such an oil by solvent extraction from a stock of 0·850 v.g.c. the stock must be cut to approximately 0·916 sp. gr. 60°/60° F., or slightly above 300° C. b.p. at 10 mm.

In connexion with solvent extraction studies, Hunter and Nash [10, 1935] and others have developed graphic methods of correlating solvent extraction data in which the specific gravity is of importance. A particularly convenient and direct method of plotting solvent-oil phase diagrams on the basis of per cent. solvent and either specific gravity or viscosity-gravity constant which has been in use by the Atlantic Refining Company since 1932 was published by Kurtz [12, 1935].

(*c*) Refractive Index in the Examination and Classification of Lubricating Oils.

At the present time the refractive index is rarely used in the routine examination of lubricating oils. The usual opinion has been that the refractive index is roughly proportional to the density and that there is no good reason for taking the refractive index. This point of view is now definitely out of date. It is probable that as knowledge concerning the real composition of lubricating fractions is accumulated it will become standard practice in the thorough examination of lubricating fractions to determine the refractive index and dispersion.

This will be discussed more fully in connexion with the section on Analysis of Lubricating Oil. An indication of the possible usefulness of refractive index data may be gained by calculating the refractivity intercepts of lubricating oil boiling under 10 mm. Hg pressure at 220° C. as indicated in Table III. The following refractivity intercept values are obtained:

Pennsylvania	1·0481
Mid-Continent	1·0482
Gulf Coast no. 1	1·0497
„ no. 2	1·0472
„ no. 3 (Mirando)	1·0523

TABLE III

Refractive Index and Density of Cuts of American Lubricating Oils [8, 1925]*

Boiling-point at 10 mm.	*Pennsylvania dewaxed*		*Mid-Continent dewaxed*		*Gulf Coast no. 1*		*Gulf Coast no. 2*		*Gulf Coast no. 3*	
	$d^{20°}_{4°}$	$n^{20°}_{D}$	$d^{20°}_{4°}$	$n^{20°}_{D}$	$d^{20°}_{4°}$	$n^{20°}_{D}$	$d^{20°}_{4°}$	$n^{20°}_{D}$	$d^{20°}_{4°}$	$n^{20°}_{D}$
140	0·818	1·4562	0·841	1·4668	0·867	1·4788	0·886	1·4874	0·900	1·4954
180	0·830	1·4627	0·857	1·4757	0·887	1·4913	0·906	1·5003	0·925	1·5118
220	0·843	1·4696	0·873	1·4847	0·900	1·4997	0·924	1·5092	0·948	1·5263
260	0·857	1·4771	0·887	1·4941	0·913	1·5061	0·937	1·5162	0·970	1·5367
300	0·871	1·4830	0·897	1·5015	0·922	1·5110	0·942	1·5207	0·990	1·5462
340	0·880	1·4885	0·915	1·5090	0·930	1·5181	..	..	..	..

* Interpolated on enlarged curves.

TABLE IV

Physical Properties of Original Oil, Wax, Sulphur-dioxide Extract, and 'Water-white' Oil, A.P.I. Project 6 [18, 1935]

Cut no.	*Original oil*				*Wax*				*Sulphur-dioxide extract*				*'Water-white' oil*				*Refractive index n^{25}_{D}*	*Weight (g.)*
	Kinematic viscosity		*Density*		*Kinematic viscosity*		*Density*		*Kinematic viscosity*		*Density*		*Kinematic viscosity*		*Density*			
	150° F. (Stokes)	*210° F. (Stokes)*	*150° F. (g. per ml.)*	*210° F. (g. per ml.)*	*150° F. (Stokes)*	*210° F. (Stokes)*	*150° F. (g. per ml.)*	*210° F. (g. per ml.)*	*100° F. (Stokes)*	*210° F. (Stokes)*	*100° F. (g. per ml.)*	*210° F. (g. per ml.)*	*100° F. (Stokes)*	*210° F. (Stokes)*	*100° F. (g. per ml.)*	*210° F. (g. per ml.)*		
23	0·094	0·0460	0·854	0·835	0·0615	0·0330	0·783	0·761	1·89	0·0807	0·989	0·948	0·214	0·0422	0·849	0·804	1·4684	3,134
24	0·103	0·0452	0·856	0·836	0·0705	0·0354	0·794	0·773	1·72	0·0828	0·987	0·963						
25	0·113	0·0480	0·858	0·837	0·0735	0·0379	0·799	0·799	2·60	0·0915	0·983	0·950	0·257	0·0465	0·847	0·802	1·4704	2,512
26	0·119	0·0523	0·859	0·839	0·0825	0·0400	0·800	0·780	2·72	0·0942	0·983	0·956						
27	0·128	0·0536	0·860	0·840	0·0822	0·0410	0·800	0·781	4·12	0·113	0·992	0·948	0·300	0·0498	0·850	0·809	1·4709	2,944
28	0·138	0·0575	0·862	0·842	0·0893	0·0473	0·805	0·784	4·57	0·125	0·991	0·955						
29	0·138	0·0583	0·863	0·843	0·0902	0·0518	0·805	0·786	6·79	0·137	1·013	0·982	0·328	0·0547	0·850	0·821	1·4733	2,189
30	0·143	0·0588	0·859	0·839	0·0925	0·0457	0·804	0·783	3·37	0·118	0·971	0·932						
31	0·176	0·0687	0·865	0·844	0·104	0·0498	0·813	0·792	191	0·359	1·067	0·990	0·409	0·0604	0·857	0·831	1·4739	2,214
32	0·213	0·0828	0·870	0·850	0·118	0·0555	0·812	0·792	..	..								
33	0·256	0·104	0·873	0·856	0·131	0·0777	0·819	0·799	28·5	0·268	0·993	0·950	0·591	0·0785	0·856	0·819	1·4743	1,608
34	0·311	0·108	0·877	0·857	0·173	0·0736	0·826	0·806	..	..								
35	0·329	0·114	0·879	0·859	0·187	0·0785	0·829	0·810	64·7	0·383	1·007	0·960	0·757	0·0882	0·860	0·825	1·4771	958
36	0·446	0·146	0·884	0·865	..	0·0835	..	0·807	..	..								
37	0·557	0·160	0·886	0·867	..	0·0976	..	0·817	384	0·712	1·032	0·970	0·824	0·0952	0·862	0·825	1·4772	505
38	0·648	0·187	0·891	0·870	..	0·1102	..	0·818	..	..								
(*a*)	From silica gel hold-up points (see text and Fig. 4)			23–8					2·80	0·122	0·972	0·955	0·605	0·0715	0·878	0·841	1·4909	1,423
(*b*)				29–32					6·60	0·187	0·967	0·936	0·584	0·0769	0·866	0·826	1·4815	595
(*c*)				33–8					8·78	0·255	0·949	0·912	1·13	0·1096	0·873	0·845	1·4861	1,693
					Total wax = 20·25 kg.				Total extract = 17·93 kg.				Total 'water-white' oil = 1,978 kg.					

The low value of Gulf Coast oil no. 2 relative to Gulf Coast oils nos. 1 and 3 as well as to Pennsylvania and Mid-Continent indicates that this lubricating oil is relatively rich in saturated cyclics, whereas Gulf Coast nos. 1 and 3 are relatively more aromatic. At present it is difficult to check the validity of such a conclusion because methods of analysing lubricating oil are still in a state of development.

(*d*) Specific Gravity and Refractive Index in the Analysis of Lubricating Oils for Paraffinic, Naphthenic, and Aromatic Hydrocarbons.

The development of analytical methods for determining the composition of the high-boiling petroleum fractions, such as lubricating oil, has been hindered by the lack of physical property data on pure compounds of high molecular weight. A paper by L. A. Mikeska [17, 1936] (of the Standard Oil Development Company, Bayonne, N.J.) contains extensive tables of data on such compounds. The analysis of lubricating oil will enter a new era when there are available in the literature physical property data for a variety of pure compounds of 250 to 450 molecular weight.

The American Petroleum Institute Project no. 6 (carried on at the Bureau of Standards in Washington, D.C.) is now engaged in the systematic separation of Mid-Continent lubricating oil into components [18, 1935]. Table IV indicates the thoroughness with which the preliminary work is being carried out. Eventually this programme will yield much fundamental information, and will result in the development and improvement of many methods of separating hydrocarbons.

Of the older work, that of Mabery deserves especial mention because it provided much needed data in the early days of petroleum research. Mabery's procedure was usually to distil to 200° C. at atmospheric pressure, and from there up to 300° C. at 30 mm. The fractions were thoroughly acid treated, caustic washed, and dried with calcium chloride. Formulae were assigned to the fractions on the basis of carbon and hydrogen analyses and molecular weight determinations. In his later work Mabery used selective solvents as an aid in separating high-boiling materials. Table V gives much of his data for compounds containing 15 and more carbon atoms. Mabery determined refractive indices at 25° C. in part of his work, therefore many refractive indices for which temperatures were not given have been assumed to have been taken at 25° C., and have been corrected to 20° C. on that basis.

M. Bestushew [3, 1931] records densities and refractive indices for lubricating-oil fractions before and after treatment with 2½ to 3 vol. of 98 to 100% sulphuric acid at room temperature. Naphthenic acids were removed from the stock with sodium hydroxide before the initial properties were obtained. On the basis of the initial and final properties and the percentage loss in treating, Bestushew calculated the physical properties and carbon and hydrogen analyses of the materials which had been removed. These materials he identifies as aromatic, whereas the material which did not react in his sulphuric acid treatment he calls naphthenic. His data are given in Table VI. In his discussion he places most emphasis on carbon and hydrogen ratio rather than on density and refractive index, and concludes that lubricating oils contain rings with side-chains, the number of rings per molecule increasing with molecular weight.

TABLE V

Data on Petroleum Fractions obtained by C. F. Mabery

	Source	*Ref.*	*Formula*	*Mol. wt.**	$d_{4°}^{20°}$	$n_D^{20°}$
C_nH_{2n}	Ohio	[5, 1913]	$C_{15}H_{30}$	210	0·819	1·448
	Canadian	,,	,,	,,	0·818	1·452
	Ohio	,,	$C_{16}H_{32}$	224	0·824	1·451
	,,	,,	$C_{17}H_{34}$	238	0·832	1·454
	Pennsylvania	,,	$C_{19}H_{38}$	266	0·820	1·451
	,,	,,	$C_{23}H_{46}$	322	0·855	1·471
	,,	,,	$C_{24}H_{48}$	336	0·858	1·473
	,,	,,	$C_{26}H_{52}$	364	0·856	1·472
C_nH_{2n-2}	Ohio	[14, 1923]	$C_{15}H_{28}$	204	0·861	1·467
	California	[5, 1913]	$C_{16}H_{30}$	222	0·879	1·472
	Texas	,,	,,	,,	0·888	1·469
	,,	,,	,,	,,	0·890	1·486
	,,	,,	$C_{17}H_{32}$	236	0·895	1·474
	Louisiana	,,	,,	,,	0·880	1·478
	Ohio	,,	$C_{19}H_{36}$	264	0·845	1·463
	Texas	,,	,,	,,	0·900	1·495
	Ohio	,,	$C_{21}H_{40}$	292	0·853	1·467
	,,	,,	$C_{22}H_{42}$	306	0·860	1·471
	,,	,,	$C_{24}H_{46}$	334	0·862	1·473
	Pennsylvania	,,	$C_{27}H_{52}$	376	0·867	1·474
	,,	,,	$C_{28}H_{54}$	390	0·868	1·482
C_nH_{2n-4}	Louisiana	,,	$C_{16}H_{28}$	220	0·875	1·483
	,,	,,	,,	,,	0·894	1·485
	Ohio	[14, 1923]	,,	218	0·865	1·469
	California	[5, 1913]	$C_{17}H_{30}$	234	0·898	1·480
	Louisiana	,,	,,	,,	0·902	1·490
	Ohio	[14, 1923]	,,	226	0·865	1·474
	California	,,	$C_{18}H_{32}$	248	0·898	1·484
	Louisiana	,,	,,	,,	0·906	1·494
	Ohio	,,	,,	244	0·878	1·473
	Louisiana	[5, 1913]	$C_{19}H_{34}$	262	0·917	1·499
	Ohio	[14, 1923]	,,	258	0·868	1·475
	,,	,,	$C_{20}H_{36}$	270	0·870	1·477
	Louisiana	[5, 1913]	$C_{21}H_{38}$	262	0·915	1·500
	Ohio	,,	$C_{23}H_{42}$	318	0·882	1·482
	,,	,,	$C_{24}H_{44}$	332	0·885	1·482
	,,	[14, 1923]	,,	334	0·879	1·481
	,,	[5, 1913]	$C_{25}H_{46}$	346	0·889	1·483
	,,	[14, 1923]	,,	348	0·879	1·484
Materials non-volatile at 300° C. and 30 mm. of Hg and insoluble in alcohol and ether	Pennsylvania	[15, 1927]	$C_{38}H_{66}$	633	0·886	1·505
	,,	,,	$C_{61}H_{114}$	851	0·898	1·502
	Ohio	,,	$C_{36}H_{62}$	493	0·905	1·511
	,,	,,	$C_{66}H_{112}$	908	0·898	1·505
	Mid-Continent	,,	$C_{37}H_{64}$	510	0·904	1·505
	,,	,,	$C_{58}H_{110}$	803	0·912	1·510
	,,	,,	$C_{62}H_{112}$	856	0·929	1·498
	,,	,,	$C_{33}H_{50}$	477	0·909	1·514
	Texas	,,	$C_{36}H_{64}$	502	0·930	1·494
	,,	,,	$C_{35}H_{58}$	482	0·926	1·496
Fractions from high-boiling cuts which are soluble in alcohol and ether	Cabin Creek	[14, 1923]	$C_{22}H_{40}$	309	0·871	1·494
	West Va.	,,	$C_{52}H_{100}$	717	0·879	1·490
	,,	,,	$C_{58}H_{112}$	803	0·881	1·483
	Embelton, Pa.	,,	$C_{28}H_{52}$	384	0·875	1·495
	,,	,,	$C_{32}H_{60}$	438	0·877	1·491
	,,	,,	$C_{37}H_{70}$	518	0·879	1·890
	Sour Lake	,,	$C_{33}H_{54}$	450	0·936	1·500
	Texas	,,	$C_{39}H_{66}$	531	0·949	1·498
	,,	,,	$C_{62}H_{112}$	849	0·959	1·496
	Baku, Russia	,,	$C_{27}H_{44}$	381	0·914	1·494
Fractions from high-boiling cuts which are insoluble in alcohol and ether	Cabin Creek	,,	$C_{33}H_{58}$	459	0·868	1·490
	West Va.	,,	$C_{54}H_{100}$	750	0·882	1·489
	,,	,,	$C_{122}H_{232}$	1,696	0·901	1·483
	Embelton, Pa.	,,	$C_{40}H_{72}$	549	0·870	1·494
	,,	,,	$C_{58}H_{106}$	805	0·882	1·489
	,,	,,	$C_{125}H_{234}$	1,730	0·903	1·489
	Sour Lake	,,	$C_{44}H_{72}$	602	0·942	1·499
	Texas	,,	$C_{56}H_{88}$	792	0·965	1·496
	Baku, Russia	,,	$C_{80}H_{140}$	1,098	0·935	1·493

* Molecular weights, ref. [5], are calculated from formula; refs. [14, 15] are experimental values, some obtained in stearic acid and some in benzene.

S. Kyropoulos [13, 1929] and Davis and McAllister [4, 1930] have developed methods of analysing lubricating oil based on density and molecular weight or boiling-point. These workers tabulated a limited amount of pure compound data, mainly for compounds of less than 200 molecular weight, and on the basis of series relations for these low molecular weight compounds, interpreted as well as

TABLE VI

Data of M. Bestushew on Lubricating-oil Fractions from Russian Crudes

Crude source or type	Boiling-point at pressure X, ° C.	Pressure X in mm. of Hg	Description*	Density, $d^{20°}_{4°}$	Refrac. index, $n^{20°}_{D}$	Empirical formula
Grosney crude containing paraffin	145–75	5	A	0·855	1·4738	$C_{18}H_{33\cdot9}$
			B	0·822	1·4543	$C_{18}H_{37\cdot3}$
			C	0·966	1·538	$C_{15}H_{20}$
	175–205	5	A	0·870	1·4835	$C_{20}H_{36}$
			B	0·835	1·4600	$C_{20\cdot9}H_{41\cdot2}$
			C	0·956	1·5428	$C_{18}H_{26\cdot6}$
	215–45	5	A	0·903	1·4957	$C_{25\cdot6}H_{45}$
			B	0·858	1·4710	$C_{26}H_{50\cdot3}$
			C	0·986	1·5520	$C_{24\cdot6}H_{32\cdot9}$
	245–75	5	A	0·907	1·5028	$C_{27\cdot7}H_{47\cdot9}$
			B	0·870	1·4759	$C_{28\cdot1}H_{52\cdot7}$
			C	0·99	1·5598	$C_{26\cdot7}H_{37}$
Balachany crude	155–85	6	A	0·876	1·4860	$C_{17\cdot3}H_{30\cdot7}$
			B	0·847	1·4671	$C_{17\cdot5}H_{33\cdot7}$
			C	0·976	1·5406	$C_{16\cdot6}H_{22\cdot2}$
	225–55	6	A	0·908	1·5022	$C_{23\cdot5}H_{41\cdot9}$
			B	0·885	1·4824	$C_{24\cdot1}H_{45\cdot5}$
			C	0·976	1·5504	$C_{22\cdot8}H_{31\cdot8}$
	250–80	6	A	0·919	1·5060	$C_{26\cdot2}H_{45\cdot7}$
			B	0·893	1·4892	$C_{26\cdot5}H_{49\cdot7}$
			C	0·996	..	$C_{25\cdot1}H_{34\cdot6}$
	266–96	6	A	0·921	1·5065	$C_{28\cdot1}H_{49}$
			B	0·895	1·4894	$C_{28\cdot8}H_{53\cdot6}$
			C	0·996	..	$C_{26\cdot1}H_{36\cdot4}$
Kalushsky crude	159–80	6	A	0·889	1·4901	$C_{16\cdot2}H_{28\cdot1}$
			B	0·860	1·4679	$C_{17\cdot5}H_{33\cdot3}$
			C	0·956	1·5372	$C_{12\cdot3}H_{18}$
	180–201	6	A	0·899	1·4974	$C_{18}H_{29\cdot8}$
			B	0·862	1·4892	$C_{19\cdot8}H_{37\cdot7}$
			C	0·966	1·5521	$C_{14\cdot7}H_{18\cdot7}$
	223–44	6	A	0·927	1·5162	$C_{22\cdot8}H_{37}$
			B	0·878	1·4775	$C_{24\cdot6}H_{46}$
			C	0·986	1·5635	$C_{20\cdot3}H_{26\cdot8}$
	244–65	6	A	0·943	1·5200	$C_{27\cdot4}H_{42\cdot7}$
			B	0·895	1·4823	$C_{28\cdot1}H_{52\cdot2}$
			C	1·006	1·5700	$C_{23\cdot7}H_{34\cdot1}$
	265–86	6	A	0·949	1·5208	$C_{28\cdot2}H_{45\cdot6}$
			B	0·904	1·4860	$C_{29\cdot8}H_{54\cdot9}$
			C	1·006	..	$C_{26\cdot1}H_{33\cdot1}$
Maikop crude	178–214	11	A	0·885	1·4885	$C_{18\cdot6}H_{31\cdot8}$
			B	0·837	1·4604	$C_{20}H_{37\cdot6}$
			C	0·976	1·5407	$C_{15}H_{19\cdot5}$
	250–86	11	A	0·913	1·5051	$C_{25\cdot6}H_{44}$
			B	0·868	1·4736	$C_{27\cdot9}H_{51\cdot5}$
			C	0·976	1·5501	$C_{22\cdot5}H_{34\cdot5}$
	286–315	11	A	0·920	1·5145	$C_{24\cdot9}H_{40\cdot6}$
			B	0·885	1·4790	$C_{31\cdot4}H_{59}$
			C	0·976	1·5733	$C_{27\cdot1}H_{41\cdot2}$
Surachany crude	211–48	7	A	0·861	1·4794	$C_{18\cdot8}H_{34\cdot2}$
			B	0·836	1·4615	$C_{19\cdot4}H_{36\cdot4}$
			C	0·966	..	$C_{14\cdot3}H_{20\cdot2}$
Dossor crude	206–42	6	A	0·882	1·4867	$C_{22\cdot4}H_{39\cdot9}$
			B	0·863	1·4748	$C_{22\cdot8}H_{44}$
			C	0·966	1·5411	$C_{18\cdot2}H_{23\cdot9}$
	277–313	6	A	0·893	1·4932	$C_{32\cdot1}H_{55\cdot6}$
			B	0·873	1·4793	$C_{32\cdot4}H_{46\cdot8}$
			C	0·996	1·5610	$C_{25}H_{32}$

* A = Original fraction free from naphthenic acids.
B = Residue after treatment with 2½–3 vol. 98-100% H_2SO_4 at room temperature. Called naphthenes.
C = Properties calculated for material removed by acid on assumption that properties are additive. Called aromatics.

they could data for lubricating-oil fractions of 300 to 450 molecular weight. Their methods may become more generally used when physical property data for pure compounds of high molecular weight are available, so that less extrapolation will be required. The data on lubricating oil tabulated by Kyropoulos is given in Table VII.

TABLE VII

Miscellaneous Data on Refractive Index of Lubricating Oils

Description	Ref.	Mol. wt.*	$d^{20°}_{4°}$	$n^{20°}_{D}$	Aniline point
Valvoline oil, AAAX	[13, 1929]	825	0·8874	1·4916	..
,, ,, EH	,,	760	0·8874	1·4920	..
,, ,, special heavy	,,	650	0·8820	1·4891	..
,, ,, H	,,	603	0·8818	1·4884	..
,, ,, XRM	,,	612	0·8806	1·4880	..
,, ,, MA	,,	500	0·8725	1·4840	..
,, ,, ML	,,	413	0·862	1·4774	..
,, ,, WLB	,,	427	0·858	1·4752	..
,, ,, M8	,,	295	0·8437	1·4663	..
Veedol a	,,	466	0·8944	1·4989	..
,, b	,,	488	0·8944	1·4988	..
Harley-Davidson	,,	554	0·9016	1·4996	..
Texaco oils, Ford	,,	354	0·9305	1·5131	..
,, ,, light	,,	346	0·9304	1·5137	..
,, ,, medium	,,	362	0·9328	1·5149	..
,, ,, heavy	,,	382	0·9357	1·5158	..
,, ,, super heavy	,,	462	0·9366	1·5163	..
,, ,, Russian oil HM	,,	424	0·9396	1·5165	..
,, Mobil Arctic	,,	351	0·9225	1·5117	..
,, ,, A	,,	410	0·9245	1·5118	..
,, ,, BB	,,	470	0·9258	1·5114	..
Pennsylvania lubricating oil	[21, 1935]	512	0·8760	1·4877	111·8
Same, hydrogenated	,,	511	0·8632	1·4750	121·0
Naphthenic base oil	,,	349	0·9690	1·5420	52·6
Same, hydrogenated	,,	352	0·9235	1·4989	90·4
Oil no. 1	,,	334	0·9419	1·5251	62·0
Oil no. 1, hydrogenated	,,	339	0·8932	1·4858	94·0
Oil no. 2	,,	419	0·9089	1·5019	92·2
Borneo oil dist. charge stock	[23, 1934]	342	0·9995	1·5642	40·0
SO_2 and benzene extract	,,	317	1·0399	1·59	(−15)
,, ,, raffinate	,,	398	0·9484	1·5206	75·2
Fractions of charge stock:	,,				
Cuts 15·7% by vol. 1		287	1·0005	1·5654	20·2
,, ,, 2		320	1·0048	1·5690	26·2
,, ,, 3		336	1·0033	1·5668	32·5
,, ,, 4		354	1·0005	1·5640	35·0
,, ,, 5		377	0·9978	1·5610	43·8
,, ,, 6		383	..	1·5594	..
Fractions of raffinate (38·2% of charge):	,,				
Cuts 13·3% by vol. 1		331	0·9454	1·5141	63·5
,, ,, 2		378	0·9505	1·5198	68·2
,, ,, 3		399	0·9501	1·5200	72·2
,, ,, 4		418	0·9503	1·5201	76·4
,, ,, 5		447	..	1·5228	78·6
,, ,, 6		446	0·9555	1·5214	82·0
Fractions of residue (55·3% of charge):	,,				
Cuts 14·6% by vol. 1		262	1·0163	1·5845	..
,, ,, 2		379	1·0348	1·5973	..
,, ,, 3		293	1·0399	1·6018	..
,, ,, 4		302	1·0424	1·6032	..
,, ,, 5		319	1·0377	1·6033	..
,, ,, 6		344	1·0437	1·600	..

* Molecular weights, refs. [13, 23], by cryoscopic method using benzene.
,, ,, ref. [21], ,, ,, ,, ,, naphthalene.

By far the most thorough work directed towards a practical method of determining the composition of lubricating oil is that of Waterman and his associates [20, 1935; 23, 1934; 24, 1935]. In this work great reliance is placed on refractive index and refractive dispersion measurements.

These workers have used the atomic refraction constants of Eisenlohr (C = 2·418, H = 1·10) and calculate the Lorentz-Lorenz specific refractions of naphthenes and paraffins. Fig. 2 shows the relation between specific refraction and molecular weight, and is used for determining the weight per cent. of naphthene rings and paraffin chains in aromatic-free oil obtained by hydrogenation.

Their complete method calls for (1) repeated hydrogenation until the specific dispersion $(n_{G'}-n_C)/d$ is less than 158, which assures complete hydrogenation; (2) measurement of n_D^{20} and d_4^{20} on the product; (3) determination of molecular weight; (4) evaluation of per cent. naphthene and per cent. paraffin with Fig. 2.

The per cent. of aromatic material in the original sample is arrived at from the change in aniline point during hydrogenation, i.e. 1° C. rise in aniline point = 0·85% by weight of aromatic rings. This is subtracted from the percentage of naphthene in the completely hydrogenated sample in evaluating the original composition.

Table VIII shows the application of this method to the study of the extraction of Borneo oil distillate with sulphur dioxide. It is clear that the method is laborious and time-consuming, but it is by far the best method of analysing lubricating oil that has thus far been developed.

Specific Gravity of Asphalts, Coal Tars, and Bituminous Substances

(*a*) Asphalts and Bituminous Substances.

The monumental work of Herbert Abraham [1, 1929] on Asphalts and Allied Substances is so complete and so authoritative that it should be consulted by any one wishing complete information on the relation between specific gravity and other properties of asphalts. Table IX gives specific gravities, viscosities, and fusibilities of bituminous substances according to the date and classification of Abraham. Table X gives specific gravities for unblown and blown asphalts from various crudes.

For many purposes asphalts with specific gravities above 1·0 are preferred, since such asphalts have no tendency to flow upwards when submerged in water. Most asphalts have specific gravities between 1·000 and 1·150, but refined Trinidad asphalt may have a gravity as high as 1·4, which is about the same as that of bituminous coal, or that of the heaviest horizontal gas-retort tar pitch.

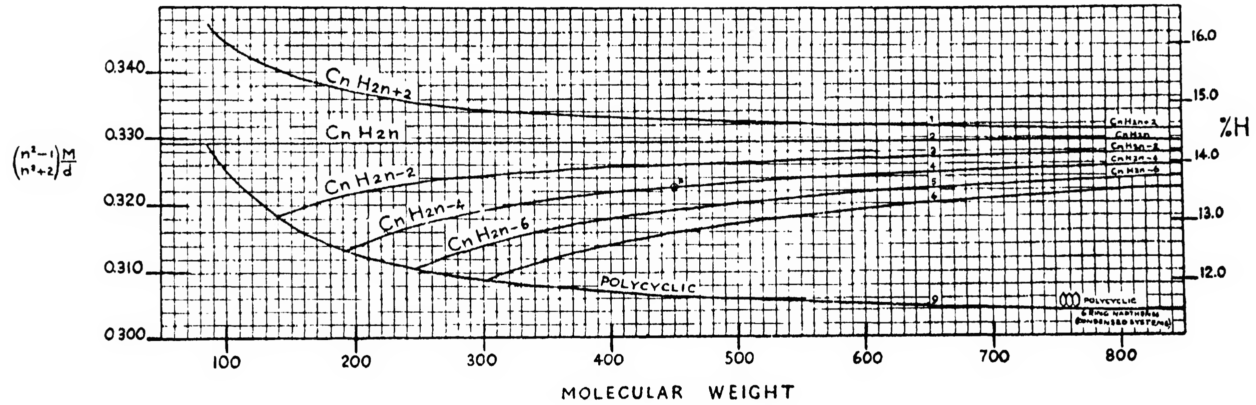


FIG. 2.

TABLE VIII

Application of Waterman's Analysis to the Study of Sulphur Dioxide and Benzene Extraction of Borneo Oil Distillate

	Ultimate analysis															
		%C	%H	*x*	n_x^t	*t*	d_4^t	*t*	$\frac{n^2-1}{n^2+2}\frac{1}{d}$ *for D line*	*t*	*Mol. wt. in benzene at f.p.*	*Aniline point*	$\frac{n_{G'}-n_C}{d}\times 10^4$	*% paraffinic chains*	*% naphthenic*	*% aromatic rings*
Charging stock, Borneo oil dist.	..	..	..	D	1·5642	20	0·9995	20	0·3255	20	342	40	..	35	25	40
Charging stock completely hydrogenated	observed	86·5	13	C	1·4973	20	0·9281	20	0·3170	20	342†	87·8	152	35	65	0
	calculated*	87·0	13	D	1·5001	20	..	..	..	..	..	..	..	..	..	..
		..	..	F	1·5063	20	..	..	..	..	..	..	..	..	..	..
		..	..	G′	1·5115	20	..	..	..	..	..	..	..	..	..	..
$SO_2+C_6H_6$ refined product (38·2% wt.)	observed	87·7	12·1	D	1·5077	50	0·9290	50	0·3207	50	398	75·2	..	43	39	18
Refined product completely hydrogenated	observed	86·3	13·3	D	1·4843	50	0·8962	50	0·3194	..	373	96·4	149	43	57	0
	calculated*	86·8	13·2	C	1·4752	70	0·8842	70	(0·3186)	20	..	..	..	..	..	..
		..	..	D	1·4777	70	..	..	..	..	..	..	..	..	..	..
		..	..	F	1·4836	70	..	..	..	..	..	..	..	..	..	..
		..	..	G′	1·4884	70	..	..	..	..	..	..	..	..	..	..
Extract (55·3% wt.)	observed	89·6	8·7	D	1·59	20	1·0399	20	..	..	317	..	..	34	10	56
Extract completely hydrogenated	observed	86·9	12·7	C	1·4979	20	0·9272	20	0·3175	20	306	79·0	157	34	66	0
	calculated*	87·0	13·0	D	1·5005	..	..	..	..	..	..	..	..	..	..	..
		..	..	F	1·5069	..	..	..	..	..	..	..	..	..	..	..
		..	..	G′	1·5124	..	..	..	..	..	..	..	..	..	..	..

* = Calculated from $\frac{n^2-1}{n^2+2}\frac{1}{d}$.

† Molecular weight in naphthalene.

TABLE IX

Specific Gravity of Bituminous and Related Products according to H. Abraham [1, 1929]

Genus	*Species*	*Member*	*Sp. gr. at 77° F. (of non-mineral matter)*	*Engler visc. 212° F. 100 c.c.*	*Fusibility ° F.*	*Penetration at 77° F.*
Bitumens	Petroleums	Non-asphaltic	0·75–0·90	..	< 32	Liquid
		Semi-asphaltic	0·80–0·95	..	< 32	"
		Asphaltic	0·85–1·00	..	< 32	"
	Natural waxes	Ozokerite	0·85–1·00	..	140–200	5–10
		Montan wax	0·90–1·00	..	170–200	0·5
	Natural asphalts	<10% mineral matter	0·95–1·12	..	60–325	0–350
		>10% " "	0·95–1·15	..	60–400	0–150
	Asphaltites	Gilsonite	1·05–1·10	..	250–350	0–3
		Glance pitch	1·10–1·15	..	250–350	0–5
		Grahamite	1·15–1·20	..	350–600	0
Pyrobitumens	Asphaltic pyrobitumens	Elaterite	0·90–1·05	..	Inf.	Rubbery
		Wurtzilite	1·05–1·07	..	"	0–5
		Albertite	1·07–1·10	..	"	0
		Impsonite	1·10–1·25	..	"	0
		Asphaltic pyrobituminous shales	1·50–1·75	..	"	0
	Non-asphaltic pyrobitumens	Peat (dry)	0·15–1·05	..	"	0
		Lignite (dry)	1·00–1·25	..	"	0
		Bituminous coal	1·20–1·40	..	"	0
		Anthracite coal	1·30–1·60	..	"	0
		Lignite and coal shales	1·30–1·75	..	"	0
Pyrogenous distillates	Pyrogenous waxes	Wax tailings	1·00–1·10	50–100	60–100	10–150
		Paraffin wax	0·85–0·95	25–50	100–150	5–50
	Petroleum tars	Carburetted water-gas tar	1·00–1·18	25–50	< 0–10	..
		Oil-gas tar	0·95–1·10	25–50	< 0–20	..
	Coal tars	Horizontal gas-retort tar	1·18–1·33	150–650	< 0–40	..
		Inclined " "	1·15–1·25	100–300	< 0–30	..
		Vertical " "	1·08–1·16	25–50	< 0–25	..
		Coke-oven coal tar	1·15–1·26	30–100	< 0–25	..
		Blast-furnace coal tar	0·95–1·10	75–100	< 0–25	..
		Gas-producer "	1·12–1·20	100–∞	< 0–50	..
		Low-temperature coal tar	0·95–1·12	25–50	< 0–25	..
	Wood tars	Pine tar	1·05–1·15	±65	0–50	..
		Hardwood tar	1·10–1·21	±50	0–50	..
	Miscellaneous tars	Peat tar	0·90–1·05	..	40–60	..
		Lignite tar	0·85–1·05	..	60–90	..
		Shale tar	0·85–0·95	..	60–90	..
		Bone tar	0·95–1·05	..	0–10	..
Pyrogenous residues	Pyrogenous asphalts	Residual oils	0·85–1·07	..	32–110	100–350
		Blown petroleum asphalt	0·95–1·07	..	80–400	25–200
		Residual asphalt	1·00–1·17	..	80–225	0–150
		Sludge asphalt	1·05–1·20	..	80–225	0–150
		Wurtzilite asphalt	1·04–1·07	..	150–300	2–20
	Petroleum pitches	Carburetted water-gas-tar pitch	1·10–1·25	..	80–300	0–100
		Oil-gas-tar pitch	1·15–1·30	..	80–300	0–100
	Coal-tar pitches	Horizontal gas-retort-tar pitch	1·25–1·40	..	80–212	0–100
		Inclined gas-retort-tar pitch	1·25–1·35	..	80–212	0–100
		Vertical gas-retort-tar pitch	1·15–1·30	..	80–300	0–100
		Coke-oven coal-tar pitch	1·20–1·35	..	80–300	0–100
		Blast-furnace coal-tar pitch	1·20–1·30	..	80–212	0–100
		Gas-producer-tar pitch	1·20–1·35	..	80–212	0–100
		Low-temperature-tar pitch	1·10–1·26	..	80–200	0–100
	Wood-tar pitches	Pine-tar pitch	1·10–1·20	..	100–212	0–100
		Hardwood-tar pitch	1·20–1·30	..	100–212	0–100
	Miscellaneous pitches	Rosin pitch	1·08–1·15	..	120–200	10–100
		Peat-tar pitch	1·05–1·15	..	100–250	0–100
		Lignite-tar pitch	1·05–1·20	..	80–250	0–100
		Bone-tar pitch	1·10–1·20	..	80–225	0–100
		Fatty-acid pitch	0·90–1·10	..	35–225	5–350

TABLE X

Specific Gravity of Petroleum Asphalts [1, 1929]

Type of product	*Field*	*Specific gravity 77°/77° F. for various samples*				
		1	*2*	*3*	*4*	*5*
Unblown asphalt from semi-asphaltic petroleum	Mid-Continent	1·050	1·078	1·119	1·145	..
Unblown asphalt from asphaltic petroleum	Mexican	1·015	1·024	1·036	..	..
	Trinidad	1·095	1·120	1·40	1·42	..
	Venezuela	1·082	1·105	..	..	..
	California	1·065	1·095	1·113	1·127	1·158
	Gulf Coast	1·022	1·033	..	..	..
	Japan	1·050	..	..	..	..
Blown asphalt from non-asphaltic petroleum	Lima, Indiana	0·987	1·002	1·005	1·015	1·021
Blown asphalt from semi-asphaltic petroleum	Illinois	0·958	1·010	..	..	..
	Mid-Continent	0·988	1·009	1·016	1·029	1·054
Blown asphalt from asphaltic petroleum	Mexico (Panuco)	1·005	1·015	1·022	1·037	..
	Venezuela	1·050	1·072	..	..	..
	Columbia	1·016	1·018	..	..	..
	California	1·008	1·045	1·060	1·070	..
	Gulf Coast	1·004	1·032	..	..	..

(*b*) Coal Tars.

Volkman, Rhodes, and Work [22, 1936] have recently published a thorough study of the physical properties of coal tars. Properties were determined both before and after filtering, with a pressure filter, while hot. These authors conclude that surface tension and adhesive qualities can be estimated from the specific gravity of the filtered tar since there is a linear relation between specific gravity and surface tension. Alundum extraction shells of medium porosity were used for filtration with 50-lb. pressure, the whole filtering set-up being immersed in a hot-water bath (temperature not stated). Table XI presents a small part of the data of Volkman, *et al.*

TABLE XI

Specific Gravity and Surface Tension of Filtered and Unfiltered Coal Tars [22, 1936]

Condition of tar	*Type of tar*	*Sample no.*	*Sp. gr. 25°/25° C.*	*Surface tension at 90° C. by bubble process, dynes per cm.*	*% by wt. dist. up to 300° C.*	*Consistency float test at 32° C. sec.*
Unfiltered	Vertical retort	1 V	1·154	31·5	13·7	166·5
		2 V	1·156	32·1	14 9	162·4
	By-product coke oven	3 C	1·175	35·7	16·1	184·6
		4 C	1·195	37·5	15·5	181·9
		5 C	1·207	39·8	13·4	182·0
		6 C	1·215	40·1	10·2	173·9
		7 C	1·218	39·8	13·6	183·7
	Horizontal retort	8 H	1·241	38·9	14·4	184·3
		9 H	1·270	..	18·9	176·3
Filtered	Vertical retort	1 V	1·145	31·4	13·7	160·7
		2 V	1·150	32·2	16·8	168·7
	By-product coke oven	3 C	1·172	34·9	17·1	188·0
		4 C	1·193	37·3	16·4	187·2
		5 C	1·202	39·9	17·0	171·2
		6 C	1·209	40·2	11·3	167·8
		7 C	1·207	39·9	17·3	186·2
	Horizontal retort	8 H	1·196	38·6	18·9	134·6
		9 H	1·202	38·2	22·9	110·1

REFERENCES

1. Abraham, H. *Asphalts and Allied Substances.* D. Van Nostrand & Co., New York, 1929.
2. American Society for Testing Materials Designation D. 189–30 (1930.)
3. Bestushew, M. *Erdöl und Teer,* **7,** 159 (1931).
4. Davis, G. H. B., and McAllister, E. N. *Ind. Eng. Chem.* **22,** 1326 (1930).
5. Engler-Hofer. *Das Erdöl,* **1,** 317, 343, 350, S. Hirzel (1913).
6. Ferris, S. W., Birkheimer, E. R., and Henderson, L. M. *Ind. Eng. Chem.* **23,** 753 (1931).
7. Hill, J. B., and Coats, H. B. *Ind. Eng. Chem.* **20,** 641 (1928).
8. Hill, J. B., and Ferris, S. W. *Ind. Eng. Chem.* **17,** 1250 (1925).
9. Houghton, W. F., and Robb, J. A. *Ind. Eng .Chem.,* Anal. Ed. **3,** 144 (1931).
10. Hunter, T. G., and Nash, A. W. *Ind. Eng. Chem.* **27,** 836 (1935).
11. Jackson, E. A. *Oil and Gas J.* **33,** No. 44, 16 (21 March 1935).
12. Kurtz, S. S., Jr. *Ind. Eng. Chem.* **27,** 845 (1935).
13. Kyropoulos, S. *Z. phys. Chem.* **144,** 30 (1929).
14. Mabery, C. F. *Ind. Eng. Chem.* **15,** 1235 (1923).
15. Mabery, D. F. *Ind. Eng. Chem.* **19,** 528 (1927).
16. McCluer, W. B., and Fenske, M. R. *Ind. Eng. Chem.* **24,** 1371 (1932).
17. Mikeska, L. A. *Ind. Eng. Chem.* **28,** 970 (1936).
18. Rossini, F. D. *Refiner,* **14,** 266 (1935).
19. *J.S.A.E.* **30,** 49 (1932).
20. Vlugter, J. C., Waterman, H. I., and Van Westen, H. A. *J.I.P.T.* **18,** 735 (1932).
21. ——————— *J.I.P.T.* **21,** 661, **701,** (1935).
22. Volkman, E. W., Rhodes, E. C., and Work, L. T. *Ind. Eng Chem.* **28,** 721 (1936).
23. Waterman, H. I. *J.I.P.T.* **20,** 159 (1934).
24. —— *J. I.P.T.* **21,** 701 (Aug. 1935).

LUBRICATING GREASE

By F. MACKLEY, B.Sc., M.Inst.P.T.
Refinery Manager, Stanlow Installation, Shell Refineries Ltd.

THE term 'lubricating grease' is one which is used rather loosely to include a great variety of products, which range in consistency from fluid oils to comparatively hard materials, many of which are not in a strict sense of the word true greases but may be a mere mixture or solution of various ingredients such as bitumen, petroleum jelly, mineral oil, &c., to give special lubricating properties.

True greases are mixtures of soap, usually lime or soda base, and mineral or fatty oil, with or without water, producing more or less stable emulsions of suitable stiffness; and such products represent by far the greater bulk of the grease manufactured.

It would appear that the first serious attempt to manufacture greases of consistent quality was only so recent as 70 years ago, although there is no doubt whatsoever that even before that time such simple lubricants as tallow, lard, and suet were available and were extensively used. It is also probable that soapy derivatives from such basic fats must occasionally have been used, together with other fatty or mineral oils, but it is only in comparatively recent years, with the development of the automobile and special requirements of industrial machinery, that any serious attention has been given to producing lubricating greases suitable to withstand the working conditions involved.

The early development of such greases was in the hands of families of greasemakers who worked largely by 'boiling' in open pans the greases prepared to their own closely guarded formulae and methods, and whilst a considerable amount of credit is due to them for the relatively high quality of the products, the ever-growing demands for specialized lubrication called for a more scientific handling of grease manufacture than was possible from the old type of 'grease boiler', and production in modern factories is now almost entirely under laboratory control. In a similar manner the development of suitable formulae now has a basis in a considerable amount of research into the various factors governing the properties of greases, coupled with specialized tests as to performance in actual practice or in specially designed test machines; and at the same time productive plant and equipment are under progressive development by technical experts.

The problems confronting the present-day grease manufacturer are exceedingly varied, in that he must be able to supply not only greases of all types, but greases varying widely in consistency and in other characteristics such as tenacity, stability, melting-point, and load-bearing properties. In order to facilitate the production of such a variety, the modern grease factory must therefore be capable of great flexibility, both as regards methods of manufacture and productive capacity, and must also have the necessary facilities for the easy and efficient packing of the products into suitable containers. Such a plant should therefore consist of a manufacturing building not less than three stories high to house the manufacturing units, the flow of work being arranged downwards to the ground floor, on which all packing, storage, and delivery, should be comfortably accommodated (Fig. 1). Adjunctive to the manufacturing building should be a suitable power house capable of supplying the necessary heating steam, preferably at high and low pressure, for the heating of the manufacturing kettles and melting of ingredient fats, &c. As it is also necessary to supply some means of raising the temperature of certain greases to above 250° C., provision should be made for this to be done either by direct gas heat or preferably by a hot oil circulating unit, which could be housed conveniently along with the boilers in the power house. In a typical modern factory the top floor of the manufacturing building would house the measuring tanks used for the measuring and melting of ingredient fats, oils, caustic soda solution, &c., together with necessary gear for the preparation of lime mixtures which will be used to convert the fats into lime soaps. The supply of mineral oil into these measuring vessels should be arranged by gravity flow from overhead tanks or by pumps operating on a suction manifold to tanks situated at a lower level, and storage should be available for several qualities of mineral oil.

The contents of the measuring vessels mentioned above should be made to flow into the autoclave situated on the floor below, either by gravity through a suitable filter to take out any particles of dirt or other contaminating material brought in with the fats, or preferably it could be transferred by means of a pump which would enable the autoclave to be charged under pressure if necessary. Each autoclave should be conveniently arranged to discharge by means of a swing arm on the outlet valve into either of two jacketed kettles on the floor below, which are used for finishing the manufacture of the grease. These jacketed kettles should be capable of being heated by means of high-pressure steam or being cooled by means of water through the steam jacket. The manufacturing kettles may be made to discharge directly into suitable containers for the finished grease, or preferably the grease could be pumped through a suitable fine-mesh filter, in order finally to eliminate any possibility of contaminating material, which might easily block the nozzles of certain types of plant used in modern methods of grease lubrication.

In such a manufacturing unit as the above it is desirable to make provision to by-pass ingredients from the measuring kettles direct to the manufacturing kettles if necessary, so that any method of open-pan manufacture can be employed instead of the autoclave method.

Generally speaking, it would be desirable at least to duplicate a system as is described above, in order to provide the necessary flexibility for a daily manufacturing programme, and it would be also desirable to provide at least three additional open kettles of varying sizes, one of which should be capable of high-temperature work, so as to be able to handle easily demands for special types of greases for which autoclave production is not necessary or desirable.

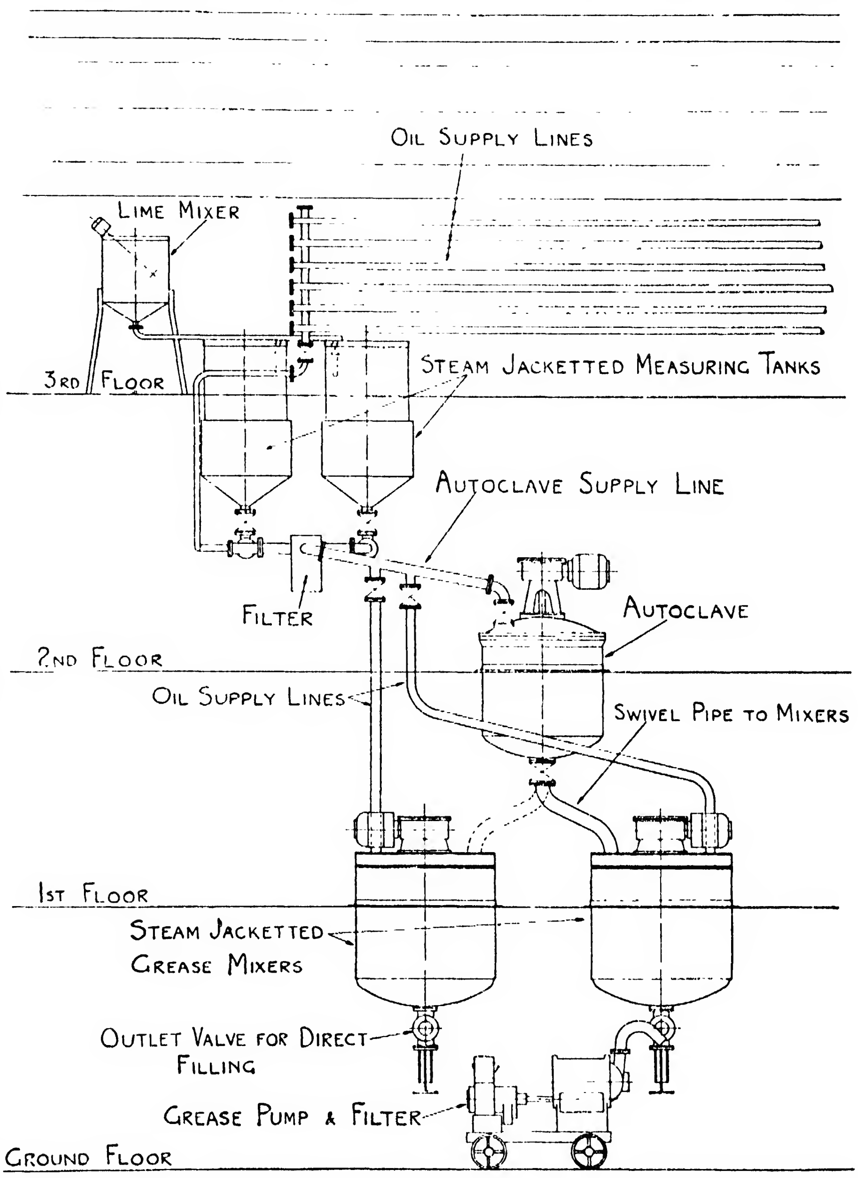
With regard to desirable features which should be allowed for in the autoclaves (Fig. 2), one of the most important is that the vessels should be capable of withstanding internal pressures of up to 150 lb. per sq. in., and if heat is supplied by means of a hot oil circulating system, the jacket should be capable of withstanding at least 50 lb. per sq. in. The internal walls of the autoclave should be smoothly fabricated, and the stirring gear, preferably of the planetary type, should be capable of a wide variation in speed up to a maximum of about 30 revolutions per minute. It is also desirable that the stirring gear should be carried on a stout frame shape to a vertical section of the vessel, and carrying spring-steel scrapers which will efficiently scrape clean the sides of the vessel on each rotation, thereby improving the heat transference and avoiding any possibility of the burning of ingredients on the side of the vessel. The stirring gear itself should consist of a series of rotating blades of such design that thorough and homogeneous mixture of the contents can readily be obtained.

The manufacturing kettles should also be designed on similar principle to those outlined above, with the exception that being open to the atmosphere they can be made of lighter construction, but in particular it is most desirable that in all vessels of this nature the continuous scraping of the sides is most desirable, both from the point of view of obtaining good manufacturing results and also for economic heating and cooling. The outlet valves on all vessels of this nature should be made flush to the bottom of the kettles so as to avoid the presence of any pocket of hard grease which might otherwise appear in the final product. Since the primary function of the autoclave is to saponify the fatty ingredients of the grease, it is not necessary to make these units as large as the final manufacturing kettles, owing to the fact that soap concentrates can be made and dilution carried out at a later stage, and therefore the autoclave can conveniently be made to operate with only half the volume of grease finally required.

With such plant available as is broadly outlined above, a variety of processes can be utilized for manufacturing purposes, since the plant can readily be operated with or without the autoclaves.

In operating with the autoclave it is possible to saponify the fatty ingredients in the presence of the whole of the mineral oil, or it is possible to saponify with only a part of the mineral oil, carrying out dilution to whatever degree is desired at a later stage, or the autoclave may be utilized for preparing the soap which may then be collected and ground if necessary for subsequent incorporation with mineral oil in the open pan.

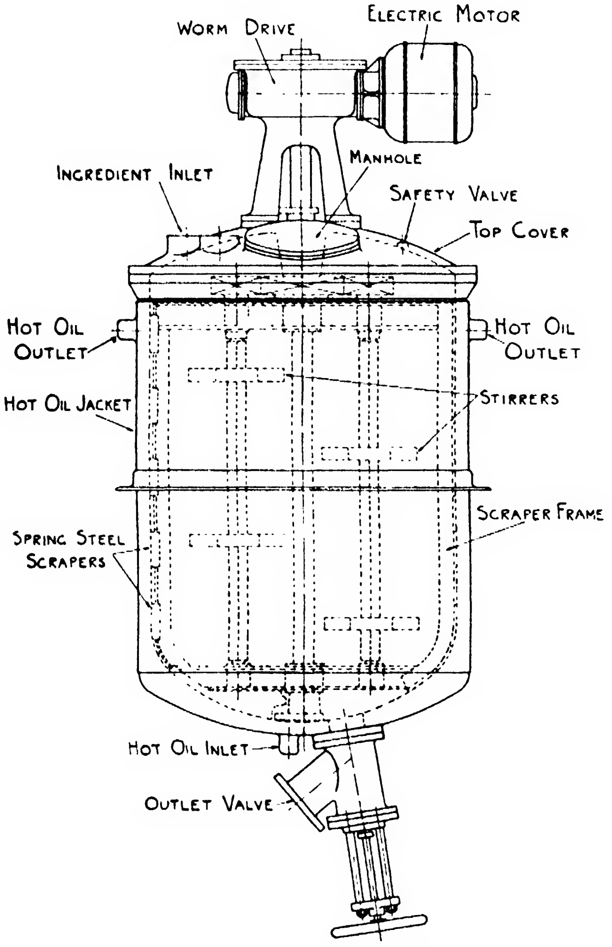
The open pans lend themselves very readily to what is known as the semi-cold process and also the more usual 'boiling' process, either at high or low temperatures, but in general it is now considered preferable to use the autoclave process wherever possible. It is a well-known fact that the reaction time for complete saponification of fat with either lime or caustic soda in the presence of water is comparatively lengthy, even at high temperatures under atmospheric pressures, and in order to obtain anything like a 100% saponification in reasonable time, it is usually necessary to employ an excess of base. The use of an autoclave will obviate this necessity since saponification can be completely carried out under pressures of, say, 80 to 100 lb. per sq. in. when using almost exactly the theoretical amount of base required, the period of time being as short as an hour or an hour and a half, depending on the nature of the fats being treated.



GREASE MANUFACTURING UNIT.

Fig. 1.

Apart from the economy in time, the obvious advantage of this method is the precision with which it can be applied and the certainty that when manufacture is completed, there will be no further slow reaction during storage which may alter the consistency and possibly the characteristics of the final grease. Furthermore, the presence of any considerable excess of base almost invariably leads to instability in the finished product, which results in the early separation of part of the mineral oil content, and avoidance of this condition is one of the marked advantages of the autoclave process. In order to obtain the best results, however, it is necessary that the ingredient fats and bases which are to be used must be brought to rigid specifications, or, alternatively, the saponification value of the stock must be continuously checked, so that due allowance may be made for any variation in these values.



Grease Making Autoclave.

Fig. 2.

Lime-base Greases.

The greater part of activities in most grease factories is concerned with the manufacture of cup greases of one type or another, these usually being greases prepared by the conversion of suitable fats into lime soap and admixture with mineral oil and water as required to give the necessary characteristics with regard to stability, consistency, colour, &c.; but under this heading may be classed a very large variety of products having widely different characteristics.

Some greases of this type are prepared in a very fluid condition and could probably best be described as soap-thickened oil, whilst others are so stiff as to require cutting into block form. Then, again, the characteristics vary very considerably according to the nature of the mineral oil used as a basis for the grease; thus it is possible by the use of an oil of low viscosity such as spindle oil to obtain a very short buttery consistency, whereas by the use of a more viscous mineral oil a much longer and sticky nature is imparted to the grease. The consistency or 'feel' may also be very largely modified by finishing off the grease either in an alkaline or acid condition; and furthermore the amount of water used in the preparation of the product also plays a very large part in affecting the above-mentioned characteristics, as well as the colour and appearance of the finished product.

The consistency and degree of gloss may be very largely modified by suitable variation of the fats used in the soap basis; and the melting-point of the grease, which is usually in the neighbourhood of 100° C., is also affected by many of the above-mentioned variables.

It will be seen from the foregoing that a very great number of variations of lime-base greases are available to those interested in grease lubrication, but whilst this may be an advantage from the point of view of satisfying the requirements of any particular machine, or part of a machine, the possibility of variations may be a serious inconvenience on the manufacturing side, and it is therefore most desirable to arrange all plant process and control with a view to obtaining constancy of results. The production of all these varieties of lime-base greases by the autoclave process will, however, follow approximately the same procedure which is broadly described below.

The fats are weighed into and melted in one of the measuring tanks referred to above, and diluted to a certain extent with a portion of the mineral oil content, after which it is transferred to the autoclave through a filter, the lines being washed through with a small quantity of the mineral oil. This is followed by a mixture or 'slurry' of the lime (which should be a very high quality finely pulverized hydrated lime) with water and some mineral oil to give a thick cream, this being followed by yet another line washing with mineral oil, so that before heat is applied the autoclaves contain a mixture of the whole of the fat, the whole of the lime, and approximately half of the final content of mineral oil. The valves of the autoclaves are then closed, and heat applied until the pressure rises to 80 lb. per sq. in., this taking about 45 min., after which the heating is continued for another 15 min., or more according to circumstances.

During this stage the fats are converted in the presence of lime and water into the lime soaps, and it would, of course, be possible to prepare such lime soaps without admixture with mineral oil, but this would be such a hard product that the soap would be difficult to incorporate homogeneously with the mineral oil in the subsequent stage. The oil which is used in the saponification stage, therefore, is used mainly as a diluent for the lime soap.

Whilst the autoclave treatment is proceeding, one of the open kettles on the floor below will have been charged with the balance of the mineral oil to complete the formula, and this will have been raised to a temperature of approximately 80° C. At the end of the saponification period the contents of the autoclave are blown down into the prepared open kettle by the developed internal pressure, and a great deal of steam admixed with glycerine fumes is then evolved owing to the high temperature. During the blowing-down period the contents of the open kettle are kept stirred very vigorously and after completion of discharge a homogeneous mixture of lime soap and mineral oil is obtained which is practically free from water at a temperature of about 115° C.

During the blowing down of the lime soap a sample is withdrawn and taken to the laboratory in order to ascertain the degree of alkalinity or acidity. In the event of a test showing the presence of free lime, sufficient fatty acids are added to the contents of the kettle to bring the contents to the predetermined value which has been found by experience to provide the most satisfactory results; and a similar adjustment is made with lime should the soap be on the acid side. The use of the autoclave, however, precludes any wide variations in this direction, providing care has been taken in the weighing of ingredients. Lime-base greases when prepared by the autoclave process may very easily be prepared to almost perfect clarity with the minimum discoloration of the ingredients during the heating process, and it would appear that the fine state of division obtained in the autoclave, coupled with the dispersive action of steam during the blowing down of the contents, is largely responsible for these satisfactory properties.

During the testing period the anhydrous grease is allowed to cool off, and when at a temperature of just over 100° C. the addition of water is commenced. The function of the water is to stabilize the mixture of lime soap and mineral oil, for without this water content such a mixture would separate into its constituents on cooling. The amount of water necessary may vary according to the formula used from between 0·4 to 2%. A considerable amount of judgement is necessary in adding the water, for it is necessary that sufficient is added to obtain the desired stability, and at the same time an excess must be avoided in order that the appearance of the grease may remain clear and transparent after cooling.

During the period when water is added the grease is continuously stirred, and it can be observed that the familiar greasy structure is developed by the continued small additions. The operative during this process will at frequent intervals remove samples of the grease into a suitable container, and stir this down until comparatively cold, in order to ascertain that the structure is as desired. When satisfactory results have been obtained the necessary amount of dye is added, together with any stabilizers which may be necessary; and after the incorporation of these ingredients the stirring is stopped whilst a sample is taken to the laboratory in order that the consistency may be determined by a rapid test. If these particulars are satisfactory the grease is ready for filling off.

It has been found advantageous in the case of certain ranges of greases, in which consistency is varied by altering the fat content, to prepare the stiffest of the range to begin with, and to draw requirements for this grade, subsequently thinning down with the prepared mineral oil, to the specifications for the thinner grades as required. This procedure not only increases the potential capacity of the kettle but also has the advantage that it is only necessary to standardize on one colour and appearance for each range of grease manufactured.

The stiffer grades are filled into the required containers whilst stirring at a temperature of 90 to 95° C., and after cooling off overnight, the batch is finally tested in the laboratory in order to ascertain that it is fully up to specification in all respects. The softer grades may be pumped through a very fine rotating filter, thus ensuring the complete absence of any small particles of soap which may not have been thoroughly incorporated, or of any adventitious solid contamination.

Other methods of manufacture of lime-base greases which may be used are the open-pan method and the semi-cold process. In the former the conversion of fat to lime soap is effected by dissolving the fats in either a part or the whole of the mineral oil, and adding a mixture of hydrated lime and water, the temperature of the kettle being raised to about 130° C. Heating is continued with frequent additions of water until the reaction between fat and lime is reasonably complete, but the time necessary is much greater than when the autoclave process is used. In fact, in order to make the lime soap in reasonable time by the open-pan method, it is usually necessary to use an excess of lime over and above the theoretical amount, but the stability of the final product is impaired by the presence of uncombined lime, and this method of manufacture is therefore avoided as much as possible. Furthermore, it is not by any means easy to control the properties of greases made by this process, and in addition the prolonged period of heating often tends to darken the colour of the mineral oils and fats used.

In the semi-cold process, greases of good appearance may be made by the judicious selection of fatty acids which may be mixed with mineral oil, after which the hydrated lime may be added in the form of a 'slurry' with a portion of the oil, the reaction being carried out at about 40° C. It is usual in this type of grease to have present a proportion of wool grease fatty acids, which appear to speed up the reaction. The final products are of pleasing appearance, although tending to be slightly granular, and also seem to be characterized by good stability, i.e. they do not readily separate oil on standing. One of the main disadvantages, however, is that reaction between the lime and fatty acids is by no means complete when the grease is filled into packages, and the grease may therefore become stiffer or alter in other properties after the material has been packed.

Fats normally used in the manufacture of lime-base greases may be glycerides, such as tallow, marrowfat, &c., or most of the commercial stearines such as cotton stearine or other vegetable derivatives, or fatty acids of animal origin. In general, it will be found that the use of high molecular weight fats or fatty acids will result in somewhat higher melting-point greases than when those of a lower molecular weight are utilized, and it is also found that unsaturated fatty acids, such as the commercial oleines, will usually result in lower melting-points than when stearines are used.

Other differences in properties are markedly noticeable by variation of the quality of fat such as higher gloss which can usually be obtained by the use of oleines, as compared with stearines, and the fact that in general a lower water content is required by the former for stabilization purposes. In the compilation of formulae for any particular purpose, a knowledge of the behaviour of the various ingredient fats is therefore essential.

The mineral oils which are normally used may vary according to the nature of the product required from certain types of spindle oil to the higher viscosity cylinder oils, but for normal production of good general purpose greases, an oil having a viscosity of Redwood 1 at 100° F. of approximately 100 sec. has been found to be generally desirable. The grease-making properties of mineral oils vary, however, not only with the viscosity, but also with the inherent properties of the oil, particularly as regards the solubility of the various lime soaps, and it is possible that these properties may ultimately be traced to differences in paraffinic or naphthenic content of the various mineral oils used.

It is usual for laboratory control of the works processes to be exercised in respect of the colour, consistency, melting-point, water content, free alkalinity or acidity, and the stability of the products; regarding the last of which it should be mentioned that the degree of stability of any particular formulae may be very definitely affected adversely by the presence of free alkali, or in certain cases may be affected favourably by the presence of small quantities of free fatty acid. The stability may also be affected by the presence of glycerine resulting from the saponification of neutral fats or may be controlled within limits by addition to the grease after manufacture, of stabilizing substances such as the higher molecular weight alcohols.

Lime-base greases of suitable consistency may be satisfactorily used for water-pump greases, cup greases, pressure gun, and ball and roller-bearing greases, and also for less specialized uses such as for axles, &c.; and as lime soap is almost insoluble in water this type of grease can be used in most circumstances where water is present, with the exception of conditions where the temperature may be approximating to the melting-point of the grease. The choice of a suitable lime-base grease for the lubrication of any particular machine must, of course, depend on the type of lubricators available, the length of feed pipe to the parts to be lubricated, and other specialized characteristics of the machine; but it may be taken that these greases can be prepared to any degree of consistency desired and to a very high degree of stability; thus providing an extremely satisfactory range for general grease-lubrication purposes. This type of grease cannot, however, be used at temperatures approximating to or exceeding 100° C., as the melting-points are usually in this neighbourhood, and for high-temperature conditions it is usual to apply one of the many types of soda soap greases which are available.

Soda-base Greases.

Certain types of soda-base grease are frequently referred to as sponge greases owing to their spongy structure, and are prepared by utilizing, in place of lime, a solution of caustic soda for the neutralization or saponification of the fats or fatty acids. The outstanding difference between these and lime-base greases is the fact that no water is required in the former in order to produce a satisfactory grease, which is, therefore, in general, a mixture of sodium soaps of selected fats, together with mineral oil base brought to a homogeneous condition in which it is reasonably stable.

These greases may be prepared by a long boiling of the fats and a portion of the mineral oil with the caustic soda, with frequent additions of water in order to assist the chemical reactions involved, and then a further addition of the balance of the oil, bringing the whole mass to a temperature of approximately 180° C. in order to drive out the small quantities of water remaining. In the older types of plant this reaction is carried out in fire or gas-heated kettles, but the process is very much speeded up by the use of autoclaves in which saponification of the fats is carried out in approximately 1½ hr. at a pressure of 120 to 130 lb. per sq. in. This very short heating period makes it possible to prepare greases of exceptionally good colour, by avoiding an appreciable darkening of the mineral oil content. After saponification is complete, the contents of the autoclave are blown down into the open kettle, which has already been heated to a temperature of 130 to 140° C. by means of superheated steam, and during the course of the blowing-down operation, most of the water and glycerine resulting from the chemical reaction between the caustic soda and fats or fatty acids is lost by flash evaporation. The contents of the open kettle are then heated for some few hours in order to drive off the remainder of the water, and subsequently allowed to cool with the requisite amount of stirring in order to impart to the grease its desirable characteristics of texture and consistency.

The appearance of most soda-base greases can be considerably modified by the degree of stirring to which they are subjected, and also by the amount of free alkali or acid which may be present; and good judgement is necessary, therefore, to ascertain at what period the stirring must be stopped. Normally such greases will present a very spongy appearance to the eye, and may be drawn out owing to their fibrous texture. If prepared with a comparatively thin basic oil the fibres tend to be rather weaker than if a more viscous oil is used, in which latter case it is possible to prepare greases having very tough and tenacious characteristics.

The melting-points of most of these greases range from 140 to 180° C., and they are therefore suitable for lubrication under comparatively high temperature conditions; but as the sodium soaps are soluble in water, the greases, with the exception of special types, are unsuitable for use where water is present, as they are rapidly washed away in the form of an oily emulsion. They may, however, be used for the preparation of oil in water-lubricating creams, but for such a process special preparations are usually necessary.

Although the usual type of soda grease has a spongy appearance and fibrous texture, it is possible, either by milling or other treatment, or even by suitable selection of fats and adjustment of the ingredients, to prepare soda greases very similar to lime-base greases in appearance, and there is some evidence that modification to a salve-like appearance is accompanied by an improvement in the stability characteristics. On the other hand, there appear to be two schools of opinion with regard to the desirable characteristics of soda greases, one being that a certain amount of oil should be released from the sponge-like soap structure; the other being that the soap should be prepared as homogeneously as possible with mineral oil, and that the lubricating properties of the soap, if any, should be utilized in practice.

Tendency for this type of grease to separate free mineral oil from the soap content is very markedly affected by the degree of dehydration to which the grease has been subjected during the course of manufacture, and in general, those greases which contain no water are most stable in this respect, even such small quantities as 0·1 or 0·2% of water, resulting in a definite tendency towards oil separation. Similarly, the presence of glycerine has an effect in this direction, although not so marked; but, on the other hand, some of the higher molecular weight alcohols appear to have a definite stabilizing effect which can also be obtained by the incorporation of certain high melting-point fatty acids. It is also to be noted that stabilization may be obtained in more or less degree by breaking down the soap fibres, either by stirring, or better still, by milling, the tendency being to produce a better degree of homogeneity. In general, there appears to be an increasing tendency towards the use of greases of more stable type having high melting-points, and there appears to be little doubt that these are more suitable for the lubrication of electrical machinery where long period runnings are involved.

In some instances, whilst the grease is being prepared certain types of fibre, such as wool or asbestos fibre, may be incorporated, in order to provide suitable pads from which the grease may be released to bearings at the approximately required rate; but such fibre sponge greases are not very extensively used. Sponge greases are very largely used for the lubrication of ball- and roller-bearings, particularly on electrical machinery, and also specially prepared types are useful for universal joints and other high-speed work where a high degree of stability is required in order to withstand the centrifugal action which tends to separate the mineral oil from the soap.

Axle Greases.

Under the description of axle greases it is usual to include some varieties which are of essentially different types, such as railway-wagon grease and tub grease. The former is prepared to meet the Railway Clearing House specifications for this type of lubricant and consists essentially of emulsions of sodium soap, free fat, and mineral oil with water, which may be present to an extent as high as 50%. The choice of fats to be used must be made very carefully in order that the products may have a suitably low melting-point and yet retain enough stiffness to prevent flowing during use. They are usually prepared by dissolving the appropriate amount of fat in the mineral oil and adding sufficient caustic soda solution during vigorous agitation, to convert a proportion of the fat into soap, the reaction being carried out at comparatively low temperatures to ensure the production of a fine and stable emulsion. Such greases are still used for the lubrication of a large amount of rolling stock, particularly on goods wagons, but, in general, grease is being superseded by oil for this purpose.

Tub greases are products which are very largely used for the lubrication of colliery tubs and for general purposes where rough lubrication is required. They are usually prepared as an emulsion of lime-rosin soap with a heavy fuel-oil base and water, which may be present to the extent of 35%. The manufacture is carried out at low temperatures by mixing fuel oil, lime, and water until a homogeneous but unstable emulsion is obtained, to which is added the rosin or rosin-oil dissolved in a small quantity of fuel oil. The amount of lime used is invariably very greatly in excess of the theoretical amount requisite to convert the rosin into soap, and the reaction is therefore fairly rapid and the grease tends to set off quickly. After thorough admixture has been ensured, the grease is therefore drawn off immediately into packages, where it is allowed to acquire its final 'set'. The degree of stiffness is usually controlled by variation of the rosin or rosin-oil content, but the variation of the water content also has a marked effect on this property.

This type of tub grease is now largely being replaced by a lubricant which is more in the nature of a soap-thickened high-viscosity oil, this type being more economical in use owing to its excellent lubricating properties, combined with the adhesiveness which prevents any flinging off during the running of the tubs.

Cart Greases.

Cart greases are prepared in a similar manner to tub greases, but, instead of using fuel oil, a lubricating-oil base is employed, and by the use of more rosin a much stiffer product is obtained, generally suitable for cart lubrication, &c.

Tallow Greases.

These are prepared as pure white products of varying degrees of stiffness, and are often favoured by engineers for heavy duty work where special conditions of lubrication are necessary. Most tallow greases contain very little or no mineral oil, but where any such oil is used it is necessary to employ a highly refined quality on account of colour requirements. The bulk of such greases is composed of high-quality tallow or other fat, part of which is converted to soap by saponification with caustic soda solution at comparatively low temperatures; together with additional fats or fatty oils which impart to the grease certain plastic properties, and increase the stability. The degree of stiffness may be controlled by varying the amount of soap in the grease, but variation of the water content also has a large effect on this property. The nature of the base used for saponification also plays an important part in determining the consistency, in that, for instance, the use of caustic potash will result in a softer and more plastic grease than when caustic soda is used. It is not unusual for this class of lubricant to be scented with a suitable odorizer such as nitrobenzene in order to mask the strong odour of the ingredients, particularly when cheap tallow is used.

Gear Greases.

Greases for open gears must possess the property of adhesiveness in order that the grease may follow the gears; and they must also be sufficiently fluid to ensure freedom of flow under the required operating conditions. In addition they must be free from any tendency towards instability. For most open gears the above-named conditions can be met by a graded series of bituminous compounds ranging from almost fluid products to comparatively hard substances. It is usual to employ, for such a range, a high-grade unblown bitumen together with a high viscosity mineral oil, varying the percentage composition to meet the requirements of viscosity, which is the control property during manufacture. As the bitumen is completely dissolved in the oil there is no danger of subsequent separation either in storage or in use. Apart from use of gear grease, some of these products find extensive use as wire-rope dressing compounds, in which capacity they serve as a lubricant as well as a protective dressing. Another type of gear grease which is available for more specialized conditions of lubrication is obtained by incorporating bitumen with sodium soap and mineral oil, the resulting products having tough and tenacious characteristics and also possessing higher melting-points than the simple type of gear grease to which reference has been made above.

Grease Blocks.

It is often necessary for greases to be supplied in definite sizes or shapes to fit into certain types of bearings, and such greases must of necessity be of a hard and solid nature. Such conditions are common in steel-rolling mills and paper mills, and it is invariably necessary that the grease in use should slowly yield a satisfactory lubricating film under the particular temperature conditions obtaining, and at the same time retain its rigidity so that the consumption may be reasonably low. It will be realized that with such a comparatively crude system of lubrication there is likely to be considerable variation of conditions between various mills, and the development of suitable greases has been correspondingly difficult. For paper-mill lubrication, a grease of very high melting-point has been developed using high-grade cylinder oil as a base, with which is incorporated the sodium soaps of rosin and wool grease. The process of manufacture must be carried out in open kettles in order to drive off all water, for which purpose the temperature is raised to 240–50° C. At this stage the grease is very fluid, and is run into metal trays in which it is allowed to cool to a solid cake of predetermined thickness. The cake is then cut up into the required sizes, wrapped, and packed in cases.

In the case of roll neck grease, it is usual to incorporate a proportion of bitumen in the composition, and wool-pitch or wool-grease soaps have also been found to be desirable constituents. Owing to the fact that water is usually being continuously poured over the roll necks when the mills are in action, it is necessary that the grease shall not be too easily soluble, and therefore it is desirable to use lime in the manufacture of the soap; but, as it is also necessary to obtain a rather higher melting-point than is attainable with lime soap, a proportion of caustic soda is also used, this proportion of soda soap also assisting in providing a thin lubricating film. This grease therefore is a typical case in which the outstanding properties of both soda and lime soaps are combined in one product to give certain desirable characteristics, and there are many other instances wherein mixed base greases are of particular value.

The method of manufacture is similar to that employed for paper-mill grease, although the temperatures employed are considerably lower, and the grease is therefore not dehydrated so completely before casting into trays.

Yet another type of grease block is tunnel grease, which is capable of giving a good lubricating film in the presence of sea-water and is used for the lubrication of tunnel shaft bearings of ships. This grease is manufactured in open kettles at a temperature of 120–30° C., using a low-viscosity mineral oil and the soda soaps of rosin and wool grease, the product containing a small percentage of water. The grease is quite solid when cold, but can easily be rubbed into a lubricating film by means of the finger. When cut into thin slices, it is quite clear, transparent, and perfectly flexible.

In addition to the foregoing types, it is not unusual to supply cup grease of stiff consistency in block form, the preparation of which follows the usual procedure for cup greases. It is necessary, however, to modify the formulae used so that an unctuous block is produced, and for this purpose such neutral fats as marrowfat may be utilized.

Aluminium-base Greases.

The greases under this class have found special application as lubricants for rocker-arms of aero engines, and also as wire-rope dressing compounds. They are prepared by incorporating a suitable percentage of aluminium stearate in a heavy mineral oil by solution at a temperature of 150° C., and then allowing to cool under special conditions. During the cooling operation the grease is a fluid possessing extraordinary tenacity and rubbery characteristics. However, after cooling and standing for some time, the rubbery property is lost and the grease sets to a transparent unctuous mass, which on reheating reverts to the rubbery condition. Owing to their remarkable tenacity these greases are finding an increasing use for gear lubrication, and there is no doubt that the special properties exhibited, together with remarkable stability, make them eminently suitable for such duty.

Lead-base Greases.

The use of lead soaps in conjunction with mineral oils has developed to a certain extent in order to meet the conditions of extreme pressure lubrication required in certain modern types of gears as used on automobiles, and it is claimed that such greases are capable of withstanding very high loads and speeds. The lead soaps may be prepared by precipitation methods, usually from lead acetate solution and sodium soaps of the appropriate fatty acids, followed by water washing or by direct saponification of fats. These soaps may then be incorporated with free fat and mineral oil to give the desired consistency, but in general, it has been found that this type of grease shows a marked tendency towards the separation of the soap.

In addition to the types of grease already described, there are numerous other products for which special claims are made but which normally are only treated by the grease manufacturer as specialities; such are the various greases of mixed bases in which various proportions of lime and soda are incorporated to modify either the water solubility or the melting-point of any particular type; or greases prepared by utilizing zinc oxide, magnesia, or barium hydroxide as bases. In general, however, the demand for such compounds is relatively small, and the production can usually be easily handled in the small experimental equipment which should be available in any modern grease factory.

Reference has been made above to the various tests which serve for controlling the manufacture and quality of the final products, and it is usually on these tests that specifications are broadly based. The colour and appearance are usually controlled by comparison with standard samples, the former directly by the use of a comparative colorimeter of suitable design, and the latter by comparing the gloss and by a general examination for freedom from contaminating particles of dirt, &c.

The consistency of most is widely determined by the use of the A.S.T.M. penetrometer, which consists essentially of an inverted metal cone of definite weight, the point of which is first adjusted to rest on the surface of the grease, and which is then allowed to drop into the mass over a definite period of time. The length of travel is accurately measured and is used as a measure of consistency.

Other methods include the substitution of a falling rod and the pumping of the grease through calibrated orifices under pressure. It is also usual in determining the consistency to specify whether the test has been carried out on the grease in its natural or 'unworked' condition, or whether the grease has been 'worked', in which latter case it is subjected to a pumping action through a perforated plate under specified conditions before the test is carried out. In a well-prepared grease the worked and unworked consistencies will approximate to the same value. The value of consistency tests is, however, essentially of an arbitrary nature, and their use can only give an approximation to those properties of plasticity, cohesion, and adhesiveness which such tests are intended to measure. It would certainly appear that consistency as determined by any of the approved methods gives only the broadest indication of performance in actual use, and its chief virtue is that it provides the manufacturer with ready means of maintaining reasonable constancy in his products.

The melting-point is usually determined by the Ubbelohde method, in which a quantity of grease is placed in a small cup, fitted to surround the bulb of a suitable thermometer, which is then inserted in a bath of liquid, the temperature of which is raised at a specified rate, the melting-point being taken as the temperature at which the grease begins to flow from the cup. Lime-base greases usually melt in the neighbourhood of 100° C., whereas soda-base greases of good type have their melting-points round about 150 or

160° C. The characteristics of the melting-point determined may be used in a measure as an indication of the stability of the grease under examination, since it has been usually found that greases which melt over a wide range of temperature are of a somewhat unstable character.

The water content of a grease may very easily be determined by admixture with a solvent of suitable boiling range, such as benzene, and subsequent distillation of the water content into an accurate measuring device.

The term 'stability' in reference to greases is largely comparative, in that most greases show some tendency to separate mineral oil on storage, and various tests have been devised in an attempt to measure this tendency. Such tests frequently involve the heating of samples to various temperatures over periods of time with subsequent standing, followed by an observation or measurement of the amount of oil separated. Other tests include subjecting the grease under test to pressure, which results in part of the mineral oil content being squeezed out in such a manner as to be capable of measurement for operative purposes, but tests of this description can only serve in a most general way towards maintaining a certain degree of stability in any particular class of product, and do not, in general, give any indication as to the behaviour of a grease in actual practice.

The tendency is, therefore, nowadays to design testing machines which will definitely give some idea of performance, and in this class of test may be placed centrifuge tests, which are used to determine the tendency to separate oil shown by greases intended for use in universal joints, &c., where high speeds are the rule; and also these tests which have been developed on definite scientific lines in order to determine the pressures to which greases may be subjected before lubrication failure sets in.

Other practical tests are carried out in spring shackles, in which the movement is controlled, and ball and roller-bearings run under definite conditions of speed, load, and temperature; the results which are obtained from such practical tests as the above provide the manufacturer with very valuable information which can be utilized in the modification either of his formulae or his methods of manufacture; and the general effect is therefore a continuous and more intensive improvement of the quality of various greases being manufactured. There still remains, however, an enormous amount of research work to be carried out on fundamental characteristics of grease, and this will undoubtedly follow the lines of a more intensive study of the internal structure of the various types, with particular reference to the spatial relationship of the molecules, whereby the micellae and soap fibres are built up. This field of investigation is a very wide one, in which little work has so far been carried out, but undoubtedly the results of such investigations would prove invaluable to the progressive grease manufacturer, who, even at the present day, is working in comparative ignorance of the true nature of his products.

APIEZON OILS

By C. R. BURCH

Metropolitan Vickers Electrical Company Ltd.

THIS name, derived from *α*-privative and *πιεξον* (pressure), was given by the Metropolitan Vickers Company to oils of very low vapour pressure produced in their laboratories by the fractional distillation of lubricating oil in a 'molecular' still. The process of molecular distillation, which was first applied to petroleum derivatives by Burch [1] in 1930, consists in heating a shallow pool or thin film of liquid, in close proximity to which is placed a cooled condensing surface. The still is exhausted to a pressure so low that the molecules of oil vapour leaving the surface of the liquid pass directly to the condensing surface without, in general, colliding with molecules of residual gas in their passage. This implies, if the distance between evaporating and condensing surfaces be 1–2 cm., that the residual gas pressure should be 0·001 mm. or less. Collisions between molecules of oil vapour and residual gas thus being of negligible number, distillation proceeds substantially as it would were the still perfectly evacuated, even although the vapour pressure of the oil at the distilling temperature may be less than the pressure of the residual gas. The distilling speed, for a pure substance, is given by $\frac{1}{4}\rho\bar{c}$ g. cm.$^{-2}$ sec.$^{-1}$, where ρ is the density of saturated vapour at the distilling temperature and $\bar{c}$ the mean molecular velocity. In round figures, for a medium molecular weight, this becomes $\frac{1}{30}$ tons per sq. yard per day for each 0·001 mm. of vapour pressure. Conversely, we can deduce the vapour pressure from the observed distilling speed, and the estimated molecular weight.

It was found possible to produce fractions from lubricating oil having vapour pressures of 0·001 mm. at 100, 200, and even 350° C. These oils made possible an advance in vacuum technique of great technical importance, for they enable us to produce a high vacuum without the aid of liquid air. The normal method of making a high vacuum had been the mercury condensation pump—a device in which a blast of mercury vapour removes the residual gas, and condensation removes the mercury vapour. Condensation on water-cooled surfaces leaves 0·001 mm. of mercury vapour uncondensed. For many purposes—e.g. thermionic valves—the pressure must not exceed 0·000001 mm., and it is therefore necessary to supplement the water-cooling by a 'trap' for mercury vapour, cooled by liquid air. It was found that suitable molecular-still fractions from lubricating oil, 1,000–10,000 times less volatile than mercury, could be boiled without decomposition at the low pressures (0·01–0·1 mm.) necessary for the vapour-blast of a condensation pump, so that by running the pump on such an oil, in place of mercury, pressures of 10^{-6}–10^{-7} mm. can be attained with water-cooling only, and liquid air is unnecessary. It then becomes practicable to exhaust vacuum devices, such as thermionic valves, continuously: the drastic heat treatment normally given to remove all adsorbed gas before sealing off from the pump is then unnecessary, and the use of ground joints (which cannot be heat treated) becomes permissible. Residues from the molecular-distillation of petroleum provide greases of extremely low vapour pressure—the Apiezon greases—with which the ground joints can be sealed.

So a new vacuum technique has arisen, in which systems demanding the highest vacua—thermionic valves and X-ray tubes—can be made easily accessible for repair or filament replacement, and can be pumped continuously while in service. Demountable valves of this type are in operation on one of the transatlantic telephone channels, and demountable high-voltage X-ray tubes are in regular use for the treatment of cancer.

REFERENCE

1. BURCH, C. R. *Proc. Roy. Soc., A*, **123** (1930).

THE USE OF ANTI-OXIDANTS IN LUBRICATING OILS

By D. A. HOWES, D.Sc., M.Inst.P.T.
Anglo-Iranian Oil Company, Ltd.

Introduction

ANTI-OXIDANTS are added to lubricating oils to suppress undesirable oxidation reactions, as in the case of similar additions to motor fuels, but there are marked differences in behaviour. In the case of motor fuels the anti-oxidants are used to prevent undesirable deterioration in storage, and these have no effect upon engine behaviour, whereas, in the case of lubricating oils, oxidation reactions proceed at a negligible rate under normal storage conditions, and the addition of anti-oxidant is not required to improve storage properties. Anti-oxidants are, however, finding rapidly increasing use in the prevention of lubricating oil deterioration under actual service conditions in the engine, where the action of oxidizing influences is unusually severe.

The changes undergone by a lubricating oil during use in an internal-combustion engine are far reaching and very complex, and the fundamental chemistry of such changes is imperfectly understood. It is true to say, however, that deterioration is brought about by the combined effects of prolonged thermal treatment and exposure to oxidizing conditions. Thermal treatment, due to contact of the lubricating oil with hot cylinder walls and pistons, results in cracking, i.e. decrease in molecular weight, and is often accompanied by the formation of carbon and certain amounts of asphaltic matter. Intensive oxidation brings about the formation of oxygenated compounds such as organic acids, asphalts, and resin and sludges. It is thus evident that after prolonged use lubricating oils become very undesirable mixtures liable to lead to serious mechanical failure. To prevent or minimize such deterioration the use of anti-oxidants has proved very efficacious. A further use of dopes in lubricating oils is the lowering of coefficients of friction and the improvement of oiliness properties. This article is limited to a consideration of anti-oxidant additions.

The Use of Anti-oxidants in Lubricating Oils

As already mentioned, lubricants usually operate under conditions favouring oxidation. Moreover, lubricating power seems to be connected in some measure with unsaturation. Further, while the presence of traces of acid may not be deleterious and, indeed, may confer that elusive property 'oiliness', the development of more acid may impart corrosiveness and all that it implies. It is evident, therefore, that lubrication provides a fertile field for the application of agents with anti-oxidant or stabilizing properties. The following discussion applies particularly to the lubricants employed in the cylinders and crankcases of internal-combustion engines where both the tendency to oxidation and the deleterious effects of oxidation are much more severe. Oil used for the big ends and main bearings of such engines is not, however, exposed to conditions leading to the formation of the hard, carbonaceous products associated with the later stages of oxidation, and in these circumstances the lubricating value of the oil may improve in use. Thus it has been found by King [8, 1933] that so long as oxidation activity is maintained, mineral lubricants of particular oxidation characteristics become possessed of the property of 'oiliness', which is considered generally to be a special attribute of the 'fixed' or fatty oils. The increase of oiliness, or lubricating value, being brought about by oxidation activity is accompanied by an accumulation of what may be described as low-temperature oxidation products. These do not diminish lubricating value, or if they do, the effect is masked by the beneficial action of the oxidation activity producing them.

The temperature of piston lubrication, on the other hand, especially in air-cooled engines, carries oxidation and/or decomposition to a much later stage, in which hard carbonaceous products are formed, and piston friction, absorbing normally about 7% of engine power, may increase to become 100% of the power developed, seizure then taking place. Lubrication seizures are familiar occurrences with small single-cylinder, two-stroke motor-cycle engines and do no damage. Great damage, however, is done when a lubrication seizure occurs in a cylinder of a multi-cylinder engine, because the free pistons are able to continue driving the engine until mechanical seizure supervenes.

The anti-oxidants developed for use in motor oils may be divided into two main classes:

1. Organo-metallic dopes.
2. Organic compounds.

1. Organo-metallic Dopes.

The best known organo-metallic compound possessing anti-oxidant properties is tetra-ethyl lead, which is used to an enormous extent as an anti-knock agent in motor fuels. This compound has also found important use in the suppression of carbonaceous deposits in lubricating oils used in engine cylinders [1, 1933]. It might be expected that such a compound would have transient action only, but experiments have shown that the effect persists for the normal life of the oil. It is very probable that the effect of lead tetra-ethyl is twofold. Its anti-oxidant effect is well known, but it may also be efficacious in virtue of its effect in raising the spontaneous ignition temperature of the oil and diminishing the tendency of the oil to crack—i.e. undergo thermal decomposition.

In tests made by King [1, 1933] the tetra-ethyl lead was added to a proprietary mineral lubricant in the form of ethyl fluid, containing lead tetra-ethyl and ethylene dibromide in the volume proportions of 60/40. The properties of the lubricant were as follows:

Sp. gr. 60° F.	0·905
Closed flash-point	430° F.
Viscosity, Redwood secs:	
at 70° F.	2,164
,, 140° F.	216
,, 200° F.	72

The following conclusions were arrived at:

(*a*) Under various conditions of treatment, such as aeration at temperatures up to 150° C. over varying periods of time, an appreciable proportion of the 1% of the added ethyl fluid remained in the oil. A new X-ray method of obtaining shadowgraphs of oil samples was employed to follow the variation of lead content.

(*b*) Journal-bearing lubrication tests performed in oxidation conditions somewhat more severe than those prevailing in an engine crankcase and in which lubricant was continuously circulated to the bearing while blown with air heated to 150° C. [9], demonstrated that the lubricant containing no lead addition became heavily impregnated with oxidation products as the trial proceeded and the viscosity increased. At the relatively low temperature of 40° C., when fluid lubrication is most probable, due to the corresponding thickness of the oil film, friction increases with time of use and increase of viscosity. The friction taken at 150° C., however, decreases by more than 50% during the time of the trial in spite of the increase of viscosity, showing the beneficial effect of oxidation activity. The two effects nearly balance at 100° C. Thus, a trial conducted in oxidizing conditions shows that at 40° C. the oil diminishes in lubricating value in use; at 100° C. the lubricating value remains nearly unchanged, while at 150° C. a remarkable improvement is exhibited. After the addition of 12 c.c. of ethyl fluid per gal. the friction at 40° C. remained constant over a 70-hr. period whereas in the absence of lead the friction increased by 25%. Whatever happens to the lead while the oil is in use, it is clear that its effect to prevent the accumulation of sludge and carbonaceous products remains.

(*c*) Oxidation experiments were carried out in glass tubes up to much higher temperatures (440° C.) in which air was drawn past asbestos soaked in oil containing various amounts of ethyl fluid. It was observed that oxidation, as indicated by the formation of steam and aldehydes, began in the case of undoped oil at 320° C., but no such indication of oxidation was observed in the presence of ethyl fluid until the temperature reached 400° C. The highest temperature reached (440° C.) did not suffice to start the flame required for complete oxidation, but the experiments with undoped oil at this temperature gave hard, carbonaceous deposits in the reaction tube, whereas oil containing 1 or 2% ethyl fluid gave no such deposits and the reaction tubes remained perfectly clear.

(*d*) Several road trials on two-stroke motor-cycle engines showed that the accumulation of carbon on the underside of the piston was much reduced using lubricating oil containing tetra-ethyl lead. At the same time trouble due to sticking of piston-rings was eliminated to a considerable extent, and the amount of carbonaceous deposits in the combustion space was much reduced. The oil remaining in the crankcase was free from sludge and deposits and had retained its original greenish sheen. There was no trace of lead deposits.

(*e*) Bench tests were also carried out on a flat twin-cylinder 500 c.c. four-stroke air-cooled A.B.C. engine, and these confirmed the results of the road tests.

Other organo-metallic substances have also been proposed and used as anti-oxidants in lubricating oils. Mardles [10] has recently published the results of extensive work on this subject, and has shown that tin compounds are particularly effective in this respect. Mardles employed a glass-bulb oxidation method and found that pronounced anti-oxidant properties were associated with many tin compounds—such as tin dioxide, tin tetraphenyl, tin ricinoleate, and tin oleate. Gold, mercury, chromium, cerium, bismuth, antimony, and many of their compounds seemed to exert little effect on the oxidation rate, although they influenced the manner of oxidation. Copper, iron, silver, vanadium, and manganese had a strong accelerating action on the rate of deterioration of all the oils examined. The effect of tin varied considerably according to the compound chosen, class of oil, conditions of experiment and concentration, but usually some beneficial action could be traced especially at temperatures below 250° C. The decreased oxidation rate was usually accompanied by less sludging, lower viscosity increase, less deposition of gum on the walls, and in general the life of the oil was prolonged.

Among the tin compounds suitable for incorporation in lubricating oils are the soluble tin fatty-acids, naphthenates, enolates, &c., also the organo-metallic derivatives such as tin-tetraphenyl, tin naphthyl, &c. Fine suspensions or colloidal dispersions of tin dust, tin dioxide, &c., may be serviceable in some circumstances, e.g. journal bearings.

The mechanism of the inhibitory action of tin compounds is not clear, but in general it would appear that these substances are capable of reacting with and destroying or reducing an active catalyst produced by the oxidation of the oil itself. This view is supported by the reduced acid values when tin compounds are present.

The use of tin compounds as anti-oxidants in lubricating oils is the subject of an English patent granted to Helmore and Mardles [6]. Up to about 1% of tin compound may be used in lubricating oil without affecting the viscosity. Possibly, as with 'leaded' oils, there may be decomposition by the action of heat to form finely divided metal, but this is said not to be injurious. As an example of the improved resistance to oxidation obtained by the addition of tin, the results of a test in which the addition of tin resulted in 40% less oxidation when a sample of lubricating oil was heated in a sealed bulb with air for 40 days are worthy of note.

The treatment has been successfully applied to castor and olive oils, oleic acid, high molecular weight hydrocarbons and mineral oils of asphalt, naphthene, and paraffin base.

Chromium compounds have also been proposed as lubricating oil anti-oxidants [5]. These, used to the extent of 0·3 to 1·0% by weight, are claimed to not only minimize the formation of deposits over the range of temperatures normally met with in internal combustion engines, but also such deposits as are formed have a soft and non-adherent character as distinct from the hard varnish-like deposits normally produced. It has also been observed, when using an oil containing small amounts of chromium oleate, that corrosion of iron and steel surfaces is less than when an untreated oil is used. Chromium compounds are effective with vegetable and blended oils in addition to oils of mineral origin.

The following metallic compounds have also been claimed to possess valuable anti-oxidant properties in lubricating oil mixtures [2]—ditolyl mercury, triphenyl bismuthine, trinaphthyl α-propyl bismuthine, dicresyl cadmium, cresyl phenyl zinc, naphthyl mercuroiodide and triphenyl stibine.

2. Organic Compounds as Lubricating Oil Anti-oxidants.

A very large number of organic compounds, particularly the hydroxy compounds and amines, have been examined for anti-oxidant effect in lubricating oils. Thus Müller [12, 1934] found that oil deterioration was delayed by the addition of 0·1% of the following compounds: nitro aniline, *p*- and *m*-phenyline diamine, urea, semi-carbazide, guanidine, and α- and β-naphthylamine. A very pronounced anti-oxidant effect was observed in the case of resorcinol, pyrogallol, phloroglucinol, α- and β-naphthol, *p*-nitro phenol, borneol, and Japanese camphor. Müller states that oxidation of lubricating oils causes the intermediate formation of peroxides and ozonides which break down to give aldehydes, acids, and lactones.

In a recent patent [3] issued to the Standard Oil Development Company claims are made for lubricants suitable for use at high temperatures (150–200° C. or even higher) incorporating 0·1% of oil-soluble inhibitors. These inhibitors consist of polycyclic aryl compounds containing an inhibitor group (NH_2 or OH) and a stabilizer group (O or S atom) attached to the same ring, e.g. 1-methyl 3-hydroxyl 4-ethyl thio benzene, 2-hydroxy 4-propyl thio naphthalene, &c.

With regard to cylinder oils and greases, the addition of less than 0·5% of a hydroxyl diphenyl compound is said to suffice to give satisfactory stability during use. The addition of 0·2–0·5% of either 2-hydroxy diphenyl or 4-hydroxy diphenyl has been specified [14].

In the case of rapeseed oil, experiments have been described [7, 1933] in which this substance was blown with air at 160° C. in the presence of various substances. Hydroquinone was effective in reducing the viscosity increase to some extent, but both anthranilic acid and phenylhydrazine were superior in this respect. Neither of these compounds prevented the development of rancidity.

Diamines such as ethylene diamine are stated to be suitable for use with oils which have to function at high temperatures, including engine oils and transformer oils [15].

More recently the proposal has been made by Mardles and Helmore to stabilize mineral and vegetable lubricants with the more weakly basic compounds normally employed as gum inhibitors in motor fuels [11]. The addition of aromatic amines and hydrazines to lubricants is not always of benefit, presumably because of their antioxidation to tar-like substances or their condensation with hydrocarbon oxidation products. However, if the basic nature of the compounds of the general formulae $RNH—NH_2$ and RNH is reduced, the results are good, if not better. For lubricants the addition of 0·25% of such compounds is usually effective, although laboratory tests should be carried out to determine the optimum concentration. In making the test, 2–5 g. of the oil are heated isothermally on the walls of a rotating cylindrical glass bulb at 225° C. for four hours and the viscosity rise (per cent.), oxygen absorption, acidity, sludge, and carbon deposition ascertained.

The following figures illustrate the results obtained with a proprietary mineral oil containing one part in 500 of different inhibitors:

	Viscosity increase %	*Acidity mg. KOH per g.*	*Carbon deposition, mg. per g.*
No inhibitor	45	24	25
Acetyl diphenylamine	26	6	18
Salicylamide	..	17	14
Phthalimide	22	..	25
Acetyl phenylhydrazine	22	8	16

The Standard Oil Development Company has recently patented lubricants containing organo-metallic compounds of the type containing two metal atoms in the molecule, e.g. Me_3-Sn-Sn-Ph_3 and similar compounds of lead, bismuth, mercury, and arsenic [4, 1933].

Sulphur compounds, such as mercaptans and disulphides, have been proposed as anti-oxidants as well as the corresponding selenium and tellurium compounds [13].

REFERENCES

1. Callendar, H. L., King, R. O., and Mardles, E. W. J. B.P. 295,230. King, R. O. *Engineering*, **136**, 183–6 (1933).
2. B.P. 433,257.
3. B.P. 442,161.
4. F.P. 789,595 (31 Oct. 1933).
5. Griffith, A. A., and Helmore, W. B.P. 423,441. Wakefield, C. C., & Co., and Evans, E. A. B.P. 431,066.
6. Helmore, W., and Mardles, E. W. J. B.P. 392,222.
7. *Ind. Eng. Chem.* **25**, 339 (1933).
8. King, R. O. *Proc. Roy. Soc.*, *A*, **139** (1933).
9. See King and Jakeman, *Aero. Research Committee*, R. and M. no. 1517.
10. Mardles, E. W. J. Technical Publication no. 2, Series C. International Tin Research and Development Council.
11. Mardles, E. W. J., and Helmore, W. E.P. 423,938.
12. Müller, H. and W. *Petr. Z.* 30 (45) (7 Nov. 1934); *Motorenbetrieb*, 7 (11), 5–6.
13. Standard Oil Development Company. C.P. 356,175.
14. U.S.P. 1,784,359.
15. U.S.P. 1,752,945 and 1,752,946.

EXTREME PRESSURE LUBRICANTS

By H. C. MOUGEY, B.Sc.

Assistant Technical Director and Chief Chemist, General Motors Corporation, Research Division, Detroit, Michigan

THE subjects of friction and of lubricants have always been complicated by the fact that different results may be obtained under different conditions, and therefore a discussion of the laws of friction or lubrication requires a statement of the conditions under which these laws are applicable. The term 'friction' is frequently used very loosely, and additional confusion may result from this fact.

Friction between surfaces is usually expressed in terms of the ratio $\frac{\text{resistance to tangential motion}}{\text{pressure normal to the surfaces}}$.

This ratio is known as the coefficient of friction, or

$$f = F/L. \quad (1)$$

From this it follows that

$$\text{The force of friction} = F = f \times L \quad (2)$$

$$\text{The work of friction} = f \times L \times s. \quad (3)$$

$$\text{The power of friction} = f \times L \times s/t. \quad (4)$$

where f = coefficient of friction, F = resistance to tangential motion, L = pressure normal to the surfaces, s = distance or space, and t = time.

The subject of friction is frequently divided into two divisions:

(*a*) Friction of dry surfaces.
(*b*) Friction of lubricated surfaces.

It should be noted that 'dry surfaces' are usually considered as those on which lubricants are not apparent by casual observation, or those which have been cleaned by more or less ordinary methods, and that 'dry surfaces' actually are coated with films of various kinds due to condensation from the atmosphere, &c.

When tests are made to determine the friction of these different surfaces under different conditions, the following general observations may be made:

Friction of dry surfaces. The force of friction

1. increases with increase of load normal to the surfaces in contact,
2. is almost independent of the area of the surfaces in contact,
3. decreases somewhat with increase of rubbing speed.

Friction of lubricated surfaces. The force of friction

1. is independent of the load normal to the surfaces in contact,
2. increases with increase of the area of the surfaces in contact,
3. increases with increase in rubbing speed.

Since the 'laws of friction' under these two sets of conditions are so different, it is apparent that there must be a third set of conditions where the laws that apply under the conditions of 'dry surfaces' change to the laws that apply under the conditions of 'lubricated surfaces', and that the laws that apply in this boundary region or 'no man's land' will probably depend upon whether the conditions more nearly approach those of 'dry surfaces' or 'lubricated surfaces'. The subject of extreme pressure lubricants covers the lubrication of surfaces when the conditions are in this boundary region, somewhere between those of 'dry surfaces' and those of 'lubricated surfaces'.

Until about 1880 the problem of lubrication, as we understand the problem to-day, did not seem to have attracted much attention. About this time Beauchamp Tower conducted his classical investigation on friction and lubrication, and discovered that considerable oil-film pressures were built up between the rubbing surfaces. A number of investigators built friction-testing machines and gave papers on testing lubricants on these machines. They pointed out the effects of viscosity, 'oiliness', design of the bearings, speed, load, &c., but at first they did not show the relation between these various factors. In 1886 Professor Osbourne Reynolds [10, 1886] presented before the Royal Society of London a mathematical theory of fluid film lubrication. Hersey [3, 1932] in 1915 showed that the coefficient of friction of a journal bearing is proportional to Zn/P (above a certain minimum value of Zn/P) in geometrically similar bearings having L/D and C/D ratios constant. Where Z is viscosity, n is the speed in R.P.M., P is the load in lb. per sq. in., L is the length of the bearing, D is the diameter of the journal, and C is the clearance between the journal and the bearing.

Other observers have shown that the minimum numerical value of Zn/P below which the relationship expressed by Hersey is no longer true, depends upon the composition of the bearing and upon the 'oiliness' of the lubricant. 'Oiliness' has been defined by Wilson and Barnard [12, 1922] as the property of lubricants by virtue of which one fluid gives a lower coefficient of friction than another fluid of the same viscosity, generally at low speeds or high loads.

It is apparent from formulae (2) and (3) that in the case of true rolling motion between two surfaces with no sliding motion whatever, the factor 's' becomes zero and that there will be no work of friction, and no resulting increase in temperature, regardless of the coefficient of friction or the amount of pressure between the surfaces, or the speed at which the rolling motion takes place. Of course, these ideal conditions are never experienced in actual service, but in the case of ordinary spiral bevel gears in rear axles of automobiles, maximum pressures and maximum sliding motion do not occur at the same time, that is, the amount of sliding motion between the surfaces of the gear teeth is small when the load is high, and as a result the requirements for a lubricant for the surfaces of the gear teeth are usually not very severe. However, if the amount of sliding motion should be sufficiently high, due to high speed or to a design which permits more sliding motion, or if the loads on the gear teeth should become sufficiently high, then the problem of lubricating the gear teeth would become more complicated, and more would be required of the lubricant. It was due to these different conditions of service that the Lubricants Committee of the Society of Automotive Engineers in 1931 gave to the lubricants that are required for these more severe conditions the name 'Extreme Pressure Lubricants'.

The Lubricants Committee recognized that although in the field of perfect 'fluid film' lubrication the load-carrying ability of a lubricant depends upon the viscosity of the lubricant and upon the viscosity only, there are other properties of the lubricant which determine its load-carrying ability in the field between 'fluid film' and 'dry surfaces'. The members of the Committee did not attempt to define these other properties or to specify how they should be determined, they simply recognized these lubricants as a definite class and named them.

Extreme Pressure Lubricants, or 'E.P.' Lubricants, as they are commonly called, are lubricants which under certain operating conditions will permit greater loads or speeds than can be carried with ordinary mineral oil of similar viscosity. It will be noted that this definition is very similar to the definition of 'Oiliness'.

It appears that 'oiliness' lubricants and 'extreme-pressure' lubricants differ only in degree, and that almost any general definition for either will include both. However, in common use 'oiliness' is usually associated with only mild increases over those obtainable with mineral oil, and 'extreme pressure' with increases of larger magnitude. 'Extreme pressure' lubricants are further divided into two classes: 'mild E.P. lubricants', and 'powerful E.P. lubricants'. In view of the commercial use of the powerful E.P. lubricants for hypoid gear lubrication, these lubricants are generally commercially known as 'hypoid lubricants'.

Typical examples of 'oiliness' lubricants are saponifiable oils and blends of saponifiable oils, and blends of saponifiable oils with mineral oils. Lubricants composed of a blend of mineral oil with a base prepared by combining sulphur with saponifiable oil may be considered as one type of 'mild' extreme pressure lubricants and a lubricant containing mineral oil together with lead soap and sulphur may be considered as one type of 'powerful' extreme pressure lubricants. These examples are only for the purpose of illustration, since there are other compositions used for lubricants in all of these classes. Organic compounds containing chlorine or phosphates are receiving much attention at the present time. However, it must be remembered that an 'extreme pressure' lubricant is defined by its performance rather than by its chemical composition.

The existence of this boundary field has been recognized for many years. In discussing the subject of 'Measurements of Friction of Lubricating Oils' before the American Society of Mechanical Engineers at their fifth annual meeting in 1884, Professor Thurston [11, 1884] said: . . . 'the friction is neither the friction of solids nor the friction of fluids, but is intermediate. In all these cases, and under these various conditions affecting the method of application, it is impossible to say what is the law. There are many laws involved; but, as Mr. Woodbury says in his paper, no algebraic expression is yet obtained, or is likely to be obtained, that will be of any great value to the engineer.'

It is on account of this fact that testing machines have been used and are being used to study lubricants in the field of 'Extreme Pressure'. However, in 1884 Dr. Arvine [1], Chemist of the Standard Oil Company, pointed out that the agreement between the results yielded by ordinary testing machines and those obtained in actual practice was unfortunately very small.

Recently, many types of laboratory testing machines [4, 1931; 5, 1931; 8, 1931; 9, 1930; 13, 1932; 14, 1931] have been proposed for evaluating or classifying E.P. lubricants. All of these testing machines will show differences in the load-carrying ability of different lubricants; but, unless the testing machine will rate the lubricants in the same relative order of merit as the lubricants are rated in service, the data obtained are not only worthless, but misleading. A laboratory testing machine cannot operate under the same conditions of pressure, rubbing velocity, temperature, &c., as are encountered under all actual service conditions. Any attempt to duplicate exact service conditions results in a design which is an exact duplicate of the service unit.

Consequently, for each laboratory testing machine a set of operating conditions must be selected which will rate the lubricants in the same order of merit as is indicated by actual service. A testing machine which has been standardized in terms of the primary service data becomes a secondary standard for determining uniformity in production and for evaluating new lubricants with respect to extreme pressure characteristics.

Much time has been spent in trying to learn how E.P. lubricants work. It appears that in order to be effective a film of some kind must be formed by some material in the lubricant reacting with the bearing surfaces, or in some other way forming a deposit on these surfaces. As examples of these actions iron sulphide may be formed on the bearing surfaces if steel bearings are lubricated with a mild E.P. lubricant containing sulphur, and a deposit of metallic copper may be formed on the bearing surfaces if steel bearings are lubricated with a mineral oil containing very fine copper powder in suspension.

Unless an opportunity is given for the material in the lubricant to react with the bearing metal and thus produce the film-forming material on the surface of the bearing, an E.P. lubricant may be found to be little, if any, better than ordinary mineral oil in load-carrying ability. This explains why different testing machines appear to give such disagreeing results, and why an E.P. lubricant that is very powerful under some conditions and with a certain bearing material may fail to show these properties under other conditions or when used with a bearing of different chemical composition. This means that an E.P. lubricant does not have a definite 'film strength', although the expression 'film strength' may be very convenient in describing the performance of a lubricant on a definite testing machine when operated under specific testing conditions.

The effect of operating conditions on the performance of extreme pressure lubricants is illustrated in the reports of the National Bureau of Standards [2, 1932; 6, 1933] covering the work which was done by them for the S.A.E. Extreme Pressure Lubricants Committee. At the time that this work was undertaken by the National Bureau of Standards, several machines of different design and operating conditions were in general use. The results obtained with these machines did not check with each other, and none of them appeared to grade the lubricants in their true order of merit when used as lubricants for hypoid or spiral bevel gears operating under very extreme conditions.

These machines were tested by the Bureau of Standards using a series of 9 lubricants that were selected to illustrate the different types of lubricants recognized at that time.

The lubricants used in these tests and their rating on the different machines, as reported in the paper before the S.A.E. are shown below in Tables I and II. The load-carrying ability of the lubricants is expressed in the ratio of load at seizure in comparison to the load at seizure of mineral oil.

It will be noted that test machines 1 and 2 give results that are in fairly close agreement and that the results on machines 3 and 4 are similar to each other, but the results on machines 1 and 2 rate some of the lubricants in a different order of merit from the results on machines 3 and 4. In addition, there is not perfect agreement between machines 1 and 2 or between machines 3 and 4. All of these machines were similar in that they consisted of a steel shaft or cylinder that rotated under load against a flat or conventional bearing. The rubbing speed varied from 6 to 400 ft. per min. Some of the machines used hardened-steel bearings and journals, while unhardened steel was used in the others. As pointed out by the authors, these differences in design, materials, and operating conditions should and did result in rating the lubricants in different orders of merit.

TABLE I

Types of Lubricants

Used by Bureau of Standards [2, 6]

Lubricant no.	*Classification*
1	Straight mineral oil S.A.E. 70
2	Mineral oil plus lard oil
3	Commercial lead-soap lubricant (non-corrosive)
4	Lead-soap lubricant free from sulphur
5	Commercial sulphurized lubricant
6	Sulphur-chloride lubricant (16⅔% base plus 83⅓% lubricant no. 1)
7	Sulphur-chloride lubricant (72% lubricant no. 6 plus 28% lubricant no. 1)
8	Castor oil, U.S.P.
9	Commercial lead-soap lubricant (corrosive)

TABLE II

Relative Loads at Seizure on Four Machines

Bureau of Standards Tests [2, 6]
Relative Loads at Seizure

Lubricant no.	*Lubricant testing-machine number*			
	1	*2*	*3*	*4*
1	1	1	1	1
2	1	1	2	1·5
3	3	4	1	1
4	2	2·5	1	1
5	2	3	3	2
6	4	5	5+	3+
7	1	..	5+	3+
8	2	2·5	2	3
9	2·5	3	5+	2

A more critical examination of the data in Table II will show that the difference in load-carrying ability of the several lubricants is essentially a difference in the rate of film formation. Lubricants 3 and 4 (lead soap without added sulphur) show strong E.P. properties on machines 1 and 2, but they are not rated any better than straight mineral oil on machines 3 and 4. It is evident that the bearing materials and the temperature resulting from the operating conditions in machines 1 and 2 are such that the E.P. film is formed before the load reaches a high enough value to cause seizure, but that in machines 3 and 4 the conditions are such that the E.P. film is so slow in forming that seizure occurs at loads no higher than those mineral oils will carry. On machines 3 and 4, in the case of lubricant 9, the sulphur which is present in addition to the lead soap forms a film at a lower load and temperature, thus preventing scoring or seizure until the film from the lead soap can be formed.

The sulphur-chloride lubricants (nos. 6 and 7) furnish another example of the effect of machine design and operating conditions on the rate of film formation. These two lubricants are identical with the exception that no. 6 contains a higher percentage of sulphur chloride base than no. 7, and as a result no. 6 carries more load than no. 7 on machine no. 1. On machines 3 and 4, however, the rate of film formation is so high with lubricant no. 7 that the full capacity of the machines is reached and consequently it is impossible to show any improvement by using lubricant no. 6.

In a like manner the differences between all the other lubricants tested on these four machines may be explained on the basis that the differences in journal and bearing materials, rubbing velocity, rate at which load is applied, and other differences in operating technique, all result in a difference in the rate of film formation.

If one or both of the rubbing surfaces should be some other metal, such as brass or bronze, the composition of the film formed by chemical action of the lubricant on the bearing surface would be entirely different, and for this reason lubricants that are especially suited for steel on steel may not be as desirable for steel on bronze. For example, saponifiable oil additions appear to be more desirable than sulphur in the case of gears consisting of steel worms with bronze worm wheels.

On account of the different results that are due to differences in design of the testing machines, physical and chemical differences in the bearing surfaces, operating conditions, &c., it is apparent that no single testing machine operated under a single set of conditions can grade lubricants for all kinds of service. The Bureau of Standards, in their work for the S.A.E. Extreme Pressure Lubricants Committee recognized this fact, and as a result they designed a new testing machine in which all of these factors can be varied over a wide range. The first experimental machine of this type is described in the paper 'Apparatus for Determining Load-Carrying Capacity of Extreme-Pressure Lubricants', by McKee, Bitner, and McKee [7, 1933].

The authors state:

> 'The testing mechanism consists essentially of two self-alining steel rolls acting under load and so mounted that each may be independently driven at various speeds. These rolls are similar to the cups of typical roller bearings. Their outer or working surfaces are ground to true cylinders and their bores or inner surfaces are ground on a taper.'

By pressing these rolls together at different rates of loading by a suitable loading device, and by operating the rolls at different speeds so that slippage occurs at the area of contact, it is possible to establish a number of sets of operating conditions. A complete test of one lubricant consists in determining the loads at which scoring or scuffing of the rolls will occur under all of the various operating conditions. It is hoped that one set of operating conditions will be found so that lubricants may be graded in accord with their performance in service with hypoid gears on high-speed passenger automobiles. Another set of operating conditions may be required to grade the lubricants in accord with performance in service with very heavily loaded hypoid gears for slower speeds, such as in the case of heavy trucks. Still another set of operating conditions may be required to grade lubricants for spiral bevel gears for passenger car service, &c.

Several experimental machines have been built; in each machine an attempt has been made to improve constructional details as the result of tests on the machines of the successive designs. It is the hope of the S.A.E. Extreme Pressure Lubricants Committee that the S.A.E. Extreme Pressure testing machine will be found to grade lubricants in the order of merit as indicated by their performance in service, and that it will be possible to obtain general acceptance of the machine in the oil and automotive industries.

Load-carrying ability is recognized as the most important property of E.P. lubricants, but they must also have other desirable properties in order to be of commercial use. They must have sufficient physical and chemical stability so that they do not cause trouble from evaporation, undue change in viscosity as the result of service, separation, gumming, corrosion, loss of E.P. properties during use, &c. Since E.P. properties result from a certain amount of chemical action between the lubricant and the bearing, care must be used in developing and selecting E.P. lubricants in order to avoid undesirable chemical action that may result in corrosion, especially under unfavourable conditions of service. Such conditions may occur due to the presence of water, which must always be recognized as a possibility in most automotive applications.

E.P. lubricants must not be expected to be a cure-all for all lubrication troubles. If the design of a machine is such that lubricant is not supplied to the bearing surfaces, then failure may occur even if E.P. lubricants are used. Thrust bearings are frequently difficult to lubricate because in many designs there is little or no tendency for the lubricant to be fed between the bearing surfaces, even if the thrust bearing is immersed in the lubricant. With such designs E.P. lubricants should not be expected to be satisfactory under continuous service-operating conditions, even though they may sometimes be satisfactory for intermittent service. It is possible that in some intermittent service an E.P. lubricant may form a film by chemical action on the bearing surfaces when the bearing is not loaded, and then the bearing may operate under load for a short time on this film.

When lubrication difficulties are caused by such high operating temperatures that the lubricant tends to oxidize and thicken so that it no longer has the proper viscosity, changing to E.P. lubricants may not cure the trouble. E.P. lubricants are usually less stable than highly refined mineral oils, and therefore, under excessive high temperature conditions they may sometimes make matters worse instead of better. The obvious remedy in such cases of high temperature oxidation trouble is to lower the temperature or to change the lubricant and replace it with fresh lubricant frequently enough to prevent the formation of the oxidized and thickened lubricant.

'Pitting' of gear teeth, especially in the case of steel worms operating on bronze worm wheels, is usually the result of fatigue failures caused by too many repetitions of loads of very high unit pressure. Breaking of gear teeth in the case of spur gears or spiral bevel gears is usually another type of fatigue failure. E.P. lubricants will probably be of little or no benefit in such cases of fatigue failure unless they act indirectly, as by lowering operating temperatures and thus increasing the resistance to fatigue failure of the gears.

Although the present interest in E.P. lubricants has been developed as a result of co-operative work by the oil and automotive industries, these lubricants are equally important in many other fields. Their industrial applications are very great and may even exceed those in the automotive field. Cutting lubricants, drawing compounds, &c., may be considered as special kinds of E.P. lubricants, and it is hoped that by the continued co-operation of the manufacturers and users of E.P. lubricants in all fields, there will be rapid developments which will be to the mutual advantage of all parties.

REFERENCES

1. Arvine, Prof. F. W. Measurement of Friction of Lubricating Oils. *Amer. Soc. Mech. Eng. Trans.* **6**, pt. 1, 160–4 (1884). (Discussion.)
2. Bridgeman, O. C. The Problem of Extreme-Pressure Lubricants. *Proc. of the Thirteenth Annual Meeting, A.P.I.* sec. 3, 114–17 (Dec. 1932). *Oil and Gas J.* **31**, 50 (17 Nov. 1932); same, abridged, *Petr. Age*, **26**, 21 (Nov. 1932); discussion, *A.P.I. Proc.* sec. 3, 130 1 (Dec. 1932).
3. Flowers, A. E. and Hersey, M. D. Lubrication Research of the Amer. Soc. Mech. Engrs. *Mech. Eng.* **54**, 269–70 (Apr. 1932). (Forty-three references are listed.)
4. Larson, C. M. Discussion of Extreme-Pressure Lubricants. *Proc. of the Twelfth Annual Meeting, A.P.I.* sec. 3, 83 (Dec. 1931).
5. —— Classifying Transmission and Rear-Axle Lubricants. *J.S.A.E.* **28**, no. 3, 321–31 (March 1931). Abstracts, *Auto. Ind.* **64**, 167–8 (31 Jan. 1931); *Nat. Petr. News*, **23**, 27 (28 Jan. 1931); discussion, *J.S.A.E.* **28**, 569–71 (May 1931).
6. McKee, S. A., Harrington, E. A., and McKee, T. R. Load-Carrying Capacity of Extreme-Pressure Lubricants. *J.S.A.E.* **32**, no. 6, 217–23 (June 1933).
7. McKee, S. A., Bitner, G. F., and McKee, T. R. Apparatus for Finding Load-Carrying Capacity of Extreme-Pressure Lubricants. *J.S.A.E.* **33**, no. 6, 402 (Dec. 1933). *Nat. Petr. News*, **25**, 21–2 (6 Sept. 1933).
8. Mougey, H. C., and Almen, J. O. Extreme-Pressure Lubricants. *Proc. of the Twelfth Annual Meeting, A.P.I.* sec. 3, 76 (Dec. 1931). *Oil and Gas J.* **30**, 109–10 (12 Nov. 1931). Same cond. *Nat. Petr. News*, **23**, 47–8 (11 Nov. 1931); excerpts, *Auto. Ind.* **65**, 758–61 (14 Nov. 1931); discussion, *Nat. Petr. News*, **23**, 38–9 (18 Nov. 1931).
9. Mougey, H. C. The Significant Properties of Automotive Lubricants. Detroit Regional Meeting. A.S.T.M. (19 Mar. 1930). In *Symposium on Developments in Automotive Materials*, 127–36. (A separate pamphlet issued by the A.S.T.M.) Abstract, *Auto. Ind.* **62**, 509 (29 March 1930).
10. Reynolds, Osborne. On the Theory of Lubrication. *Royal Soc. of London, Trans.* **177**, pt. 1, 157 (1886).
11. Thurston, Prof. R. H. Measurement of Friction of Lubricating Oils. *Amer. Soc. Mech. Eng. Trans.* **6**, pt. 1, 154–8 (1884). (Discussion.)
12. Wilson, R. E., and Barnard, D. P. The Measurement of the Property of Oiliness. *J.S.A.E.* **11**, 143–56 (Aug. 1922). *Ind. Eng. Chem.* **14**, 683–95 (Aug. 1922); abstract, *Nat. Petr. News*, **14**, 45 (15 Nov. 1922); discussion, *J.S.A.E.* **11**, 156–67 (Aug. 1922).
13. Wolf, H. R., and Mougey, H. C. Extreme-Pressure Lubricants, Correlation of Service Data with Laboratory Testing Methods. *Proc. Thirteenth Annual Meeting, A.P.I.* sec. 3, 118–30 (Dec. 1932). Same cond. *Oil and Gas J.* **31**, 58 (17 Nov. 1932); excerpts, *Auto. Ind.* **67**, 650–53 (19 Nov. 1932); Abstract, *Nat. Petr. News*, **24**, 39–40 (16 Nov. 1932); discussion, *A.P.I. Proc.* 130–1, sec. 3 (Dec. 1932).
14. Wooler, E. Observations on the Testing of Lubricants. *J.S.A.E.* 28, 53–60 (Jan. 1931); discussion, **28**, 60–5.

THE PRACTICAL SELECTION OF IMPROVED LUBRICANTS

By L. L. DAVIS, BERT H. LINCOLN, and B. E. SIBLEY
Continental Oil Company, Ponca City, Oklahoma

THE problem of selecting an oil in the laboratory for its true lubricating value is as yet unsolved; and, following the thought of an old maxim, the proof of an oil is the lubrication therewith. The physical requirements of a motor lubricant, viz. viscosity, pour test, flash, volatility, &c., are fairly well established and understood. On the other hand, the chemical characteristics—particularly those having to do with lubricating value and stability—are largely mysteries. The increase in knowledge of the mechanics of the true lubricating film has been considerable during the past few years, but the general application of that knowledge to practical lubrication has been very slow.

The increasingly severe requirements on a lubricating oil demanded by the modern powerful engine operating at high speeds and temperatures has resulted in the recognition of the need for a better lubricant. This need for a better lubricant has been answered in two general ways: improved refining methods to give better physical and stability characteristics, and the use of addition agents to improve those same characteristics as well as to add materially to the true lubricating value of the mineral oil.

In several cases these addition agents have been offered after years of research work and ample practical service tests which have proved their worth. In far too many cases, however, 'dopes' are being offered to the public for addition to motor oil—which are based on insufficient empirical tests, and are in many cases actually detrimental to the equipment in which they are used.

It has been known for many years that, under severe operating conditions, animal and vegetable oils give better lubrication than petroleum or 'mineral' oils. The first step towards an explanation of this phenomenon was the report on the work of Wells and Southcombe given before the Physical Society of London in 1919 [9], and the Society of the Chemical Industry in 1920 [15], in which they showed the improved lubrication to be due to small quantities of free fatty acids adsorbed on the metal surfaces. They suggested the addition of small amounts of free fatty acid to mineral oils to obtain the oiliness characteristics of fixed oils, and termed this their 'germ process' [10, 1920; 13, 1918, 1919].

Automotive-Engine Lubricating Requirements.

The increasing power, speed, and operating temperatures of modern automobile engines has greatly aggravated bearing troubles and has increased the difficulties of satisfactory lubrication. The increase in speed and power of automotive equipment during the past few years is too well known to call for further discussion in this article, but it will be well to consider briefly the resulting conditions which must be met by the lubricant.

Sparrow [11, 1934] shows that, at 4,500 r.p.m. under full load, the maximum load on the bearings is 2,200 lb. per sq. in. of projected area and that the unit load is 1,500 lb. for approximately half of each revolution. Increased speeds and loads of modern cars produce crankcase temperatures of 250 to 300° F., and actual film temperatures in the bearings are probably materially higher. These high temperatures decrease the viscosity of the oil and hence increase end leakage in the main bearings and starvation of rod bearings.

These changes have greatly decreased the safety factor for viscous lubrication. Dickinson and Bridgeman [3, 1933] have shown that modern conditions of load, speed, and viscosity approach, if not actually pass, the critical point between viscous and boundary lubrication.

Special alloy bearings designed to withstand these more severe conditions are of three general types: (1) copper-lead alloys, containing about 60 and 40% respectively; (2) high lead alloys, with about 2% of alkaline earth metals incorporated in 98% lead; and (3) cadmium alloys. These are superior to tin-babbitt alloys in load-carrying capacity, but are more sensitive to corrosion by oxidation products of the lubricant in service.

The Use of Addition Agents.

The increasing severity of automotive operating conditions has resulted in the need of improved lubricants and the successful development and marketing by major oil companies of oils with improved lubricating value. High film strength, if defined as the ability of a lubricant to carry high loads without bearing failure or excessive wear, is a desirable feature. However, any chemically active material will give high film strength. Thus any oil soluble material containing loosely combined halogens, sulphur, or free hydrochloric acid or sulphur or even carborundum will give very high film strength by preventing metal seizure—although the rate of wear or corrosion may be excessive. The more essential lubricating characteristics such as rate of wear, corrosiveness, volatility, sludge formation, emulsibility, &c., must not be disregarded.

The difficulty is that there are no laboratory methods of measuring true lubricating value, which include all the factors entering into the successful lubrication of a piece of equipment. A satisfactory lubricant must have the ability to carry the maximum possible loads at the maximum probable temperature without metal seizure or excessive wear; it should have low friction during the periods of thin-film operation; it must protect the metal parts against wear through metal-to-metal contact; it must form a protective film against corrosion from products of combustion or decomposition; it must be stable under the maximum possible operating conditions; it must be non-volatile, non-toxic, and odourless.

The Selection of an Addition Agent.

The selection of a satisfactory addition agent to be used to improve the over-all lubricating value of a mineral oil is no easy task. Every phase of lubrication and metal protection must be given serious consideration. Our investigations have included the synthesis and study of over 1,000 organic compounds, of which surprisingly few have proved of sufficient probable engine-lubrication value to justify detailed practical study. Four general steps are used in the selection of a compound:

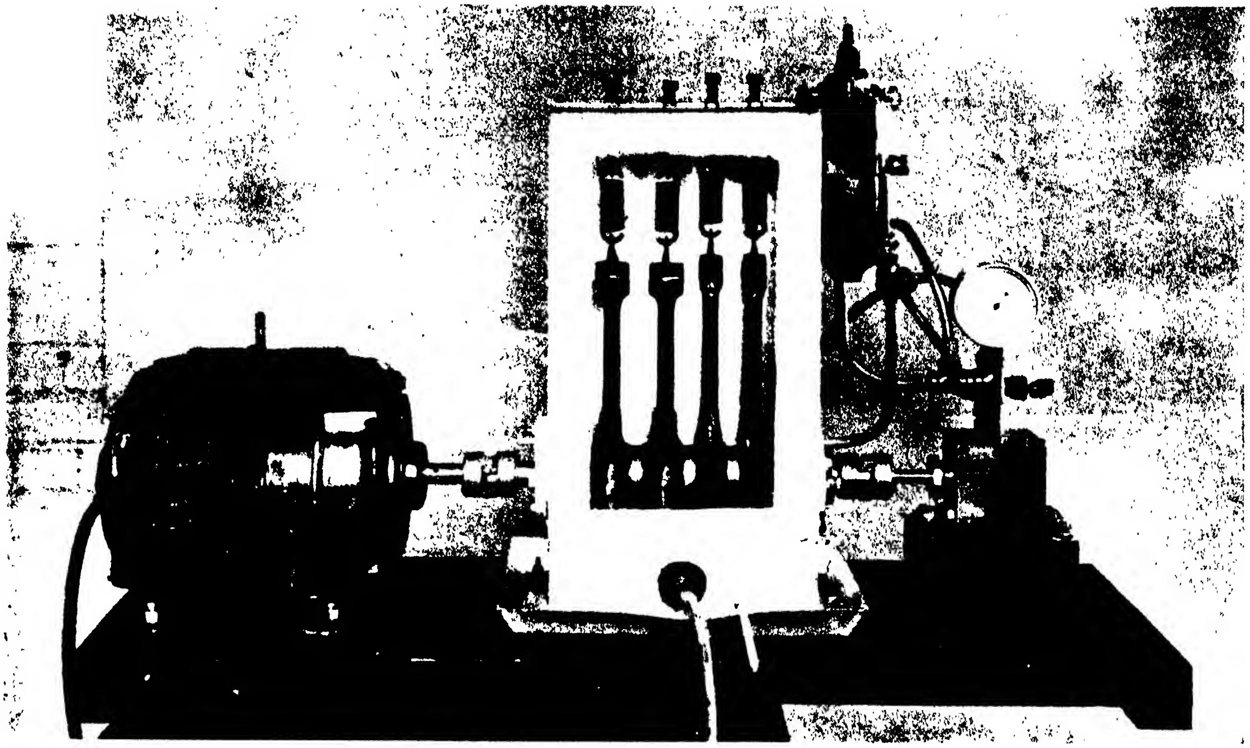


FIG. 4. Sibley connecting-rod-bearing corrosion machine

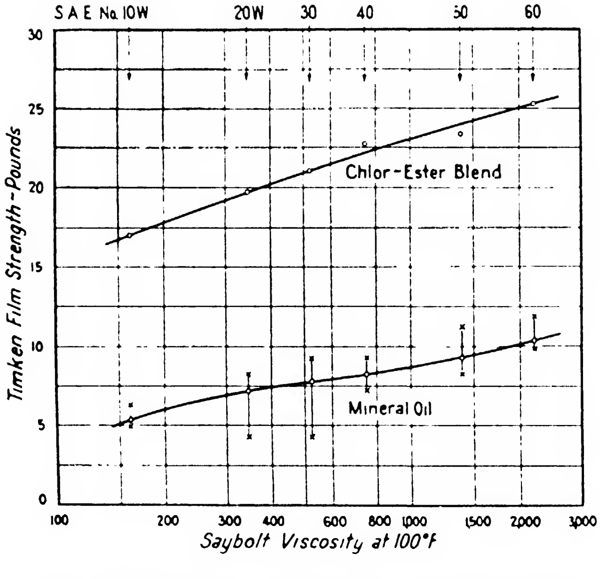


FIG. 1. Relation between Timken film strength and viscosity

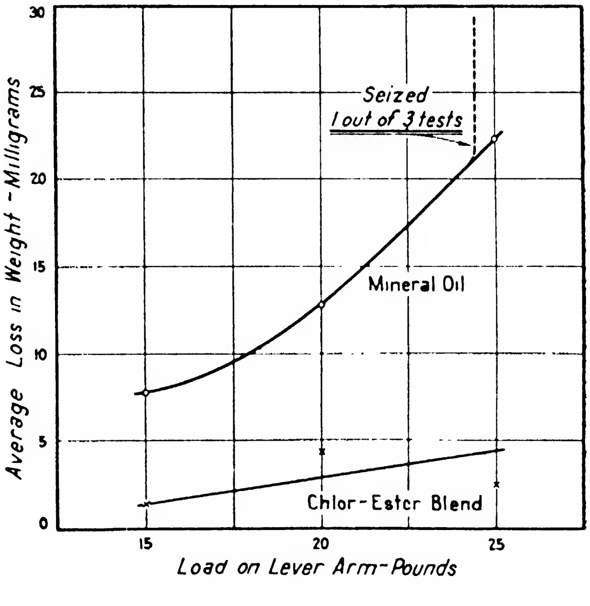


FIG. 2. Timken long-time wear tests on cadmium-silver bearing metal

1. The theoretical investigation includes the study of the physical and chemical forces of the adsorbed film on metal surfaces and the regimentation of molecules in oil solution, as discussed by Clark, Lincoln, and Sterrett.
2. Chemical laboratory study: After the synthesis and refining of a product, the chemical study—both of the pure agent and its solution in oil—considers such items as chemical and thermal stability, metal corrosion, toxicity, and effect on the oxidation stability and the physical characteristics of mineral oils produced from different types of crude and by various refining processes.
3. The physical laboratory study includes the measurement of film strength, load-carrying capacity, bearing-metal wear, oiliness, and engine-dynamometer lubrication studies.
4. Four general classes of supervised road tests have been used:
    - *a.* Controlled fleet tests.
    - *b.* Supervised commercial fleet tests.
    - *c.* Individual car tests under normal highway operation.
    - *d.* Fleet tests under American Automobile Association supervision.

Bearing failure or excessive wear occurs through the inability of the lubricant to prevent metal-to-metal contact under the given load, temperature, and speed conditions. The load-carrying ability of a lubricant is studied in the laboratory by means of the Timken [17, 1931] and Almen [16, 1932] machines.

Timken Film Strength

The Timken 'film strength' is defined as the load on the beam, in pounds, at 788 r.p.m. and at 100° F. for 10 min., which gives incipient scarring of the bearing surfaces. In order to obtain reproducible results, particularly with mineral oils which may seize due to the slight jar when the load is placed on the beam, it was found necessary to use an automatic loading device. A standard rate of 22·8 lb. per min. is used in all Timken film strength and wear tests.

The relationship between viscosity and film strength is shown in Fig. 1. The lower curve is a regular grade Mid-Continent base mineral oil and the upper curve is the same oil plus 0·75% methyl α,α-dichlorostearate [6, 1932; 14, 1934] (Chlor.-Ester). The vertical bars between the crosses represent the range in film strength of all the commercial mineral oils which we have tested. Practically every type of crude source and manufacturing process is represented. In general, we find that the greater the degree of refining, the lower the film strength of the oil from any given crude.

The Timken film strength does not consider rate of wear or corrosion and, therefore, is not an indication of what might be termed 'useful load-carrying capacity'. Long-time tests on the Timken machine indicate that the high rate of wear or 'lapping in' takes place in the early stages of the test; and that, if a lubricant will carry a given load for 90 min., it will carry that load for an indefinite period without excessive wear. A useful load-carrying-capacity test was, therefore, developed—which consists of a series of 90-min. runs on the Timken machine using progressively increasing loads until the oil fails to carry the load for 90 min. The number of minutes the last load was carried before failure is recorded. Table I shows the results of comparing a number of addition agents in 1% solutions in an S.A.E.-30 grade lubricating oil by this method. This shows that 'high film strength' when considered alone may be misleading. Thus trichlororesorcinol, with a film strength of 125 lb., is but little better than methyldichlorostearate, which has a film strength only one-fourth as high. The reason for the mineral oil and the hexyl-chloride and oleic-acid blends carrying more long-time load than their film strength would suggest is probably due to the oxidation of the oil during the series of runs previous to the final maximum-load test.

TABLE I

The Relation between Timken Film Strength and Load-carrying Capacity

Addition agent—1% added to mineral oil	*Timken film strength (lb.)*	*Load-carrying capacity*		
		No seizure (lb.)	*Seizure*	
			(lb.)	*(min.)*
S.A.E. mineral oil	8·8	10	15	1
Methyldichlorostearate	28	20	30	6
Trichlororesorcinol	125	20	30	46
Dichlorostearic acid	59	30	40	6
Dichloropropylether	44	15	20	30
Pentachloroethane	38	20	30	12
p-Chloroaniline	38	15	20	2
p-Chloroanisole	25·5	10	15	2
Chloropseudocumene	15·5	10	15	5
Hexyl chloride	8·8	10	15	2
Oleic acid	8·3	10	15	1

Timken Wear Tests on Bearing Metals

The Timken film strength as determined with steel-on-steel surfaces cannot be used to predict the effect of a given lubricant on soft bearing metals. The soft metals are used in bearings because they have the ability to continue carrying loads without metal seizure after the oil film has ruptured. Under such conditions, however, the rate of wear is excessive.

The Timken machine may be used to study this factor by using a block of the bearing metal in question and a highly polished steel cup. Wear tests of 30-min. duration were made on various bearing metals, and the weight loss in grammes of the bearing block was used as a measure of the rate of wear. A new polished cup was used for each metal and oil, but the same cup was used for the various beam loads. In all cases the cups were carefully inspected, and the better of each pair was used for the mineral oil. The results of the wear test are given in Table II. The oils used were the standard S.A.E.-30 mineral oil and the same oil plus chlor.-ester. It is interesting to note that although the mineral oil will carry relatively high loads on the better bearing metals, the resultant rate of wear is materially higher than when the same oil carries a satisfactory addition agent.

In order to counteract any possible effect of differences in the cups, a series of 6-hr. runs was made with the same cup on cadmium-silver blocks at sufficiently low loads that the cup was not changed appreciably during the series. The average results of several runs are graphed in Fig. 2. In the case of the mineral oil at 25-lb. load, failure occurred in one run out of three.

This shows that at high load, but definitely below the seizure point or film strength of either oil, the chlor.-ester blend will result in less wear than the mineral oil. Similar studies have been made with other compounding agents; and, in general, it can be said that if the product has the highly polar film-forming characteristics which give oiliness and is not corrosive on the bearing metals or copper, the rate of wear will be low.

TABLE II

Timken Wear Tests on Bearing Metals

Metal	*Oil*	*Load on beam, lb.* 20	40	60	80
		Loss in wt., g.			
S.A.E.-11 .	mineral	0·0019	0·0040	0·0058	0·0091
	chlor.-ester blend	0·0014	0·0026	0·0034	0·0071
Cadmium no. 50 .	mineral	0·0026	0·0075	seized	..
	chlor.-ester blend	0·0011	0·0056	0·0073	..
Cadmium no. 51 .	mineral	0·0025	0·0033	seized	..
	chlor.-ester blend	0·0006	0·0030	0·0047	0·0062
Copper-lead .	mineral	0·0013	0·0336	0·0390	seized
	chlor.-ester blend	0·0004	0·0035	0·0153	0·0316
Bronze no. F–1 .	mineral	0·0129	seized	..	..
	chlor.-ester blend	0·0021	0·0015	0·0046	0·0054

Photographs of the wear-test blocks for the cadmium-silver no. 51 and the bronze no. F–1 are given in Fig. 3. The failure of the cadmium-silver with mineral oil at a load of 60 lb. is particularly interesting because it indicates a possible reason for the failure of these bearings in service. The mineral oil failed to maintain a lubricating film, and the resultant frictional heat was sufficient to melt the surface of the metal which was 'wiped' out of the bearing. The chlor.-ester blend, even under 80-lb. load, maintained a sufficiently low friction to protect the bearing from failure. In the case of the bronze, the mineral oil under 20-lb. load allowed twice the wear that resulted with the chlor.-ester blend under 80-lb. load.

Almen Film-strength and Wear Tests

The results of the use of the Almen machine [16, 1932] to study a group of addition agents are given in Table III. The first column gives the standard Timken tests for purposes of comparison. The second column is the standard Almen film-strength test made with steel-on-steel at 600 r.p.m. and applying the load at the rate of 1,000 lb. per 10 sec. The 'film strength' is reported as the number of pounds per square inch of projected area the lubricant will carry for 10 sec. without seizure.

The third column is the Almen film strength using steel-on-bronze bearing metal instead of steel-on-steel. The test is conducted with the same procedure used in the regular Almen test. The fourth column gives the results of a 1 hr. wear test under a 2,000 lb. per sq. in. load. The loss in weight of the bronze pin gives the relative wear.

The fifth column records the data from a 3 hr. reversing wear test of steel-on-steel. In actual service steel-on-steel bearings and journals are not used. The sliding of rings on cylinder walls is the only place where this combination occurs. In order to study the effect of a reciprocating action, a reversing mechanism was placed on the Almen machine—so designed that the machine operated in one direction at full speed, slowed to a full stop, and then accelerated to full speed in the opposite direction with a 1¼ min. cycle between stops. The reversing wear test was run for 3 hr., and the loss in weight of the pin determined. The load was 2,000 lb. per sq. in. A study of Table III reveals that film strength alone, without consideration of wear, does not fully define a satisfactory lubricant. In general, it would appear that both high Timken steel-on-steel and high Almen steel-on-bronze film strengths are required for low wear. The only exception to this is oleic acid, which shows low wear in both tests but has poor film strength by all methods.

The excessive wear obtained with mineral oil in both wear tests indicated the desirability of studying wear at lower loads. Table IV gives the results of a series of wear tests at different loads for a mineral oil and the same oil plus chlor.-ester. Up to a load of 1,000 lb. per sq. in., the wear appears to be of the same order and within the probable reproducibility of the test. At 2,000 lb., however, the mineral oil shows excessive wear.

TABLE IV

Almen-machine One-hour Wear Tests—Steel-on-Brass

Load (lb. per sq. in.)	*Grammes loss in wt. of brass pin* *Mineral oil*	*Chlor.-ester blend*
250 . .	0·012	0·008
500 . .	0·010	0·014
1,000 . .	0·058	0·050
2,000 . .	0·859	0·040
4,000 . .	seized	0·036
6,000 . .	..	0·017
8,000 . .	..	0·009

TABLE III

Almen-machine Film-strength and Wear Tests

Oil plus 1% addition agent	*Standard Timken film strength (lb.)*	*Almen film strength, steel-on-steel (lb.)*	*Almen film strength, steel-on-bronze (lb.)*	*Almen wear tests* *Steel-on-bronze (loss in g.)*	*Reversing steel-on-steel (loss in g.)*
Mineral oil	9·3	3,500	6,000	0·586	0·451
Methyldichlorostearate	28	6,000	15,000+	0·036	0·003
Trichlororesorcinol	125	8,500	15,000+	0·006	0·003
Dichlorostearic acid	59	5,500	15,000+	0·003	0·003
Oleic acid	8·3	4,333	6,000	0·041	0·003
p-chloroanisole	25·5	5,000	5,000	0·408	0·216
Dichloropropylether	44	6,500	6,000	0·477	0·008
Pentachloroethane	38	10,000	15,000+	0·002	0·006
Chlorodiphenyl	25·5	6,500	5,000	0·757	0·008
Chloropseudocumene	15·5	4,500	5,000	0·471	0·717
Tetrachloroethylene	15·5	7,000	5,000	0·611	0·004
Hexyl chloride	8·8	5,500	15,000	0·266	0·208

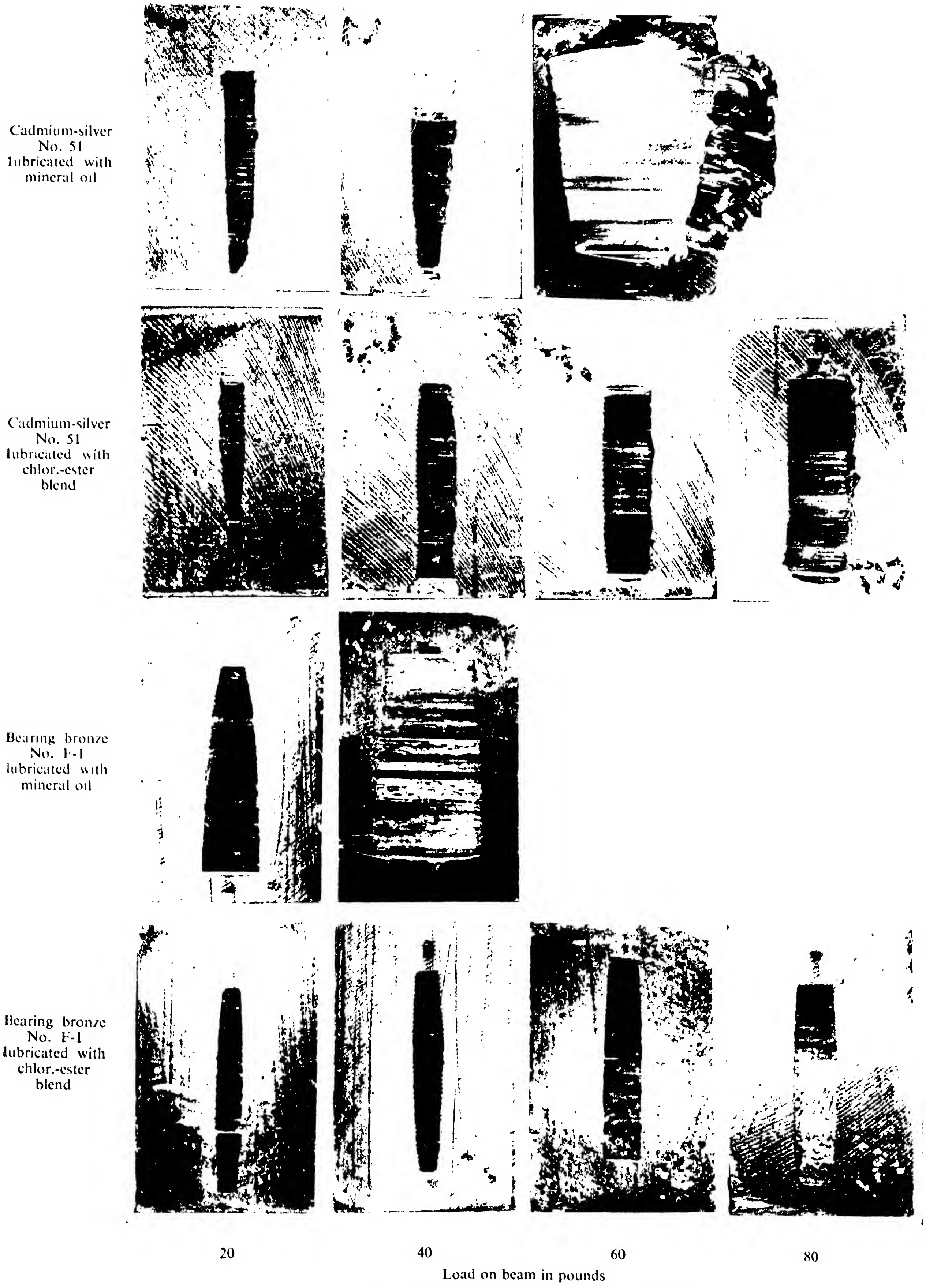


FIG. 3. Bearing-metal blocks from Timken wear test

The Almen 'film strength' is very sensitive to the speed used, and materially higher results can be obtained at lower than the designed speed of 600 r.p.m. Thus at 200 r.p.m., the chlor.-ester blend in S.A.E.–30 carries an average load of 13,000 lb., and at 160 r.p.m. over 17,000 lb.

Bearing-metal Corrosion.

It is evident that a lubricant must be non-corrosive on any metals with which it will come in contact during distribution and use. The more easily corroded metals found in automotive engines are copper and the various bearing metals, particularly those containing lead and cadmium. A study of the action of compounding agents on these metals must consider three factors:

1. They must be stable and non-corrosive in their unblended concentrated state.
2. They must not decompose in service to form corrosive materials.
3. They must not accelerate the oxidation of the mineral oil to form corrosive products, but should act preferably as oxidation inhibitors.

The first factor is easily tested by any of the usual strip-corrosion tests on the compounding agent itself. The second and third factors must be considered together, since the blended oil is used in service, and the resultant chemical activity is due to both factors. We have found the simple 'beaker' test to be of real value in forecasting the corrosion characteristics of lubricants in service. Such a test will not show small differences between oils; but, along with the other characteristics, will certainly help in discarding the large majority of questionable products. Details of this test are given elsewhere.

All types of metals found in automotive equipment, particularly bearing metals, have been studied; but we have found that a preliminary test using copper and copper-lead bearing metal will rate lubricants satisfactorily. Products which pass this test may then be tested on other metals such as cadmium-alloy or lead-alkaline earth-metal bearings. The results of the standard corrosion test on a number of lubricants are given in Table V.

The group of mineral oils is interesting in that the wide range of corrosion found on supposedly satisfactory mineral oils is surprising. The first (no. 1) is a Mid-Continent base mineral oil. The other five are extensively advertised and widely distributed brands. That this factor of corrosion by mineral oils cannot be overlooked is proved by the fact that in actual road tests with such oils copper-lead bearing failures have occurred through corrosion in 3,000 to 8,000 miles of operation.

The second group shows the corrosion resulting from various addition agents compounded with mineral-oil base no. 1. The Timken film strength is given for reference. It will be seen that a high film strength may mean a highly corrosive product.

The third group shows the corrosion test on a number of branded, commercial, compounded oils purchased on the open market. It will be seen that the majority of these products are highly corrosive.

Many corrosive agents also produce considerable sludge which may form a protective film on the test strip leading to deceptive results. In general, however, if a product shows little corrosion on both copper and copper-lead and forms no sludge, it is safe to proceed to road tests as final proof.

A connecting-rod-bearing corrosion testing machine, recently designed by B. E. Sibley, operates so as to remove any protective sludge film. This machine shown

TABLE V

Beaker Corrosion Test on Bearing Metals

Product S.A.E. 30	*Agent used %*	*Loss, mg. per 100 sq. cm.*			*Timken film strength (lb.)*
		Copper	*Copper-lead*	*Cadmium-silver*	
Plain mineral oils:					
1. Conoco Mid-Continent base	..	2	2	0·6	8·8
2. Solvent-treated Mid-Continent base	..	7 5	10	..	7·3
3. Solvent-treated Eastern base	..	10	12	..	5·3
4. Eastern base	..	7·5	23	..	8·3
5. Naphthene base	..	16	36	..	9 6
6. Eastern base	..	6·8	1·2	..	8·3
Oil no. 1 plus addition agent:					
7. Methyldichlorostearate	1	4·5	5·2	..	28
8. Pentachloroethane	1	2	2	..	..
9. Dichloropropylether	1	8	10	1·4	44
10. Trichlorophenol	1	..	15	..	49
11. Trichlororesorcinol	1	25	1	..	125
12. Triphenylchloromethane	1	77	95	0	74
13. *p*-Chloroanisole	1	69	79	0·5	26
14. Dichlorostearic acid	1	..	140	16	45
15. Oleic acid	1	..	430	485	8·3
Commercial compounded oils:					
16. Chlor.-ester blend	0·75	2·7	4·8	1·6	23
17. Isopropyl esters of oxidized wax	2	16	116	..	4·3
18. Chlorinated petroleum hydrocarbons, probably wax	..	42	65	..	21
19. Processed castor oil	5	13	150	123	10·8
20. Ketones, &c., from oxidized petroleum	..	19	40	..	15
21. Chlorinated hydrogenated fish oil	0·3*	49	153	..	19
22. Chlorinated diphenyl	0·4*	3	31	..	25
23. Chlorinated naphthalene	1·2*	2	66	..	31

* Per cent. of chlorine in blend.

in Fig. 4 consists of standard connecting rods placed on a shaft which rotates at 1,800 r.p.m. A 15-lb. load is placed on the rods by means of a spring. Oil is circulated under 30-lb. pressure from a heated sump through the drilled shaft to the bearings. A test is run for 22 hr. at 350° F. The amount of corrosion of the bearing inserts is determined as the loss of weight in grammes. Table VI shows the results of runs made on cadmium-silver and copper-lead bearings with four different oils. The difference in metal-weight loss between the chlor.-ester blend and the mineral oils is entirely too great to be explained by a difference in corrosiveness, but indicates an actual protection of the metal from corrosion. This protection must be due to the adsorbed film built up on the metal surface by the addition agent.

TABLE VI

Connecting-rod-bearing Corrosion Tests on Sibley Machine

	Weight loss in grammes				
	Continental oils		*Solvent-treated oils*		
	Chlor.-ester blend	*Mineral*	*Mid-Continent base*		*Eastern base*
			(1)	*(2)*	
Cadmium-silver bearings:					
No. 1 cap insert . .	0·0864	0·9526	1·2506	1·5801	2·1586
No. 1 rod insert . .	0·0980	0·9105	0·9724	1·4921	0·4365
No. 2 cap insert . .	0·0789	0·9818	1·7419	1·9430	1·4616
No. 2 rod insert . .	0·0709	0·8782	0·8981	1·3298	2·0556
Average loss per insert .	0·0836	0·9308	1·2158	1·5863	1·5381
Copper-lead bearings:					
No. 5 cap insert . .	0·0079	..	0·2118	0·3007	0·4387
No. 5 rod insert . .	0·0191	..	0·2673	0·2259	0·3929
No. 8 cap insert . .	0·0111	..	0·1964	0·3170	0·4484
No. 8 rod insert . .	0·0176	..	0·2153	0·2944	0·3962
Average loss per insert .	0·0139	..	0·2227	0·2845	0·4191
Length of test, hours. .	22	22	22	22½	22
Average oil pressure, lb. per sq. in. . . .	29	35	29	33	33

Bearing Protection in Service.

The primary purpose of a lubricant is the protection of bearing surfaces from wear. 'Wear' in automotive bearings results from direct chemical corrosion and mechanical abrasion. It is impossible to isolate the effects of these two factors, but it is certain that both enter into bearing wear under actual service conditions.

We have shown that the oxidation products of some mineral oils, particularly of the highly paraffinic type, are highly corrosive on the newer type of bearing metals. Actual road tests under high temperatures of operation confirm this.

The question of mechanical wear is not quite as clear. Certainly if ample oil were available at all times to furnish viscous lubrication, there would be no mechanical wear. This is proved by the fact that properly designed and lubricated industrial equipment shows practically no bearing wear. On the other hand, automotive bearings do show wear and hence must operate at times under boundary or thin-film lubricating conditions. Under such conditions the improved lubricating value obtained by a good addition agent should manifest itself in less bearing wear. Road tests to prove this must of necessity be over long periods of time, and to prove the value of the addition agent must be made in comparison between a mineral oil and the same oil with the added compound

Such comparative road tests between mineral oil and the same oil plus chlor.-ester are shown in Table VII. The connecting-rod-bearing wear is reported as the average loss of weight in grammes of all connecting-rod bearings in the car per 10,000 miles of operation. Where a 'break-in' run is reported, the freshly overhauled engine, with new bearings, was given our standard break-in run of 2,500 miles—starting at 25 m.p.h. and increasing in uniform increments to 50 m.p.h. at the end of the period. It is interesting to note that, with the exception of the dynamometer-engine tests, the rate of wear during the break-in period is materially greater than during the running period. Since the corrosion characteristics of the two oils by laboratory test are very low and of the same degree, we believe that the greater bearing metal protection of the chlor.-ester blend is due to its greater lubricating value as indicated by the wear tests discussed above. Comparative figures are not given for cadmium-silver bearings, as our study of that material is not yet complete.

TABLE VII

Rate of Wear of Connecting-rod Bearings in Service

Percentage composition of bearing metal	*Car*	*Speed*	*Rate of wear of connecting-rod bearings (g. per 10,000 miles)*	
			Mineral oil	*Chlor.-ester blend*
Copper-lead:				
Copper—58·9%	Studebaker*	Break-in	0·0924	0·0728
Lead—40%	Studebaker*	4,000 r.p.m.	0·5183	0·4569
Nickel—1·1%	Studebaker†	50 + m.p.h.	0·3424	0·1174
	Studebaker†	50 + m.p.h.	0·4232	0·2315
	Buick-8‡	50 m.p.h.	0·0544	0·0449
High lead:				
Lead—98%	Buick-8‡	Break-in	0·1864	0·1856
Alkaline-earth metals—2%	Buick-8‡	50 m.p.h.	0·1024	0·0955
Copper-lead:				
Lead—36%	Ford V-8 truck§	Break-in	0·8232	0·7112
Copper—64%	Ford V-8 truck§	50 m.p.h.	0·3781	0·2583
Cadmium-silver:				
	Pontiac, 1935‖	50 + m.p.h.	..	0·0922

* Studebaker model 'C' President engine connected to a G.E. 150-hp. dynamometer.

† Studebaker model 'C' 1934 President coupé.

‡ Conoco test fleet of Buick-8, model 33-67, 4-door sedans equipped with special bearings as noted.

§ Conoco Ford truck test fleet, Ford V-8 1½-ton trucks.

‖ Pontiac-8—1935 sedan.

Cylinder and Piston-ring Protection.

Until recently it has been generally assumed that cylinder wear results from direct abrasion between the piston-rings and the cylinder walls. More recent information indicates that it is largely the result of corrosion from the products of combustion, and that the greater part of this wear takes place during the starting period before the cylinder walls have reached a sufficiently high temperature to prevent water condensation on the surface.

True abrasion may result from distortion of cylinder walls [12, 1935] or from piston slap. However, the greatest wear is not usually across the cylinder [7, 1935]. Boerlage and Gravesteyn [1, 1932] found that in Diesel engine operation the rate of wear during the first hour was 8 times that of normal running. Duff [4, 1933] concluded that speed, load, low oil supply, high temperatures, dilution, and even abrasive content have little effect on cylinder and piston-ring wear, but that this is greatly increased by operating with cylinder-wall temperatures below 194° F. Since wear was reduced by 60 to 80%

using hydrogen as fuel, the corrosive effects of combustion products of the fuel are largely responsible for 'wear'. He showed that the use of a lubricant containing 0·6% of a vegetable acid reduced wear 25 to 40%. Everett and Stewart [5] and Keller [8, 1935], measuring wear by the iron content of the crankcase oil, found that iron is removed from the engine approximately 4 times as fast in the first hour as in the succeeding 5 hr.

In measuring the rate of wear in our laboratory, we have used the same Chevrolet engine-dynamometer assembly used for consumption tests [2, 1935]. After several flushing charges—until the flushing oil showed no iron increase—the engine stood at room temperature (85–90° F.) for 1 hr. The water jacket was cooled to 35° F. A 6-qt. charge of oil was added to the outside sump at room temperature, and the engine started under load. The cooling-water temperature was allowed to rise uniformly until the normal running temperature of 180° F. was reached in 1 hr. Typical results show the iron removal for the first hour was 0·0204 g. for the mineral oil and 0·0104 g. for the same oil plus chlor.-ester. The average rate of iron removal for the 5 succeeding hours was 0·002 g. and 0·001 g. per hr., respectively. Thus a decided advantage is indicated in the use of a carefully selected, strongly polar addition agent in a lubricant entirely separate and in addition to any lubrication value resulting from its film strength and oiliness.

Cylinder Protection in Service.

Cylinder and piston-ring wear was determined by car- and fleet-test work in connexion with the development of new addition agents. The results of three such runs are given in Table VIII. The actual ring wear as determined by loss in weight is substantial, and in all cases shows a materially greater wear for the mineral oil than for the chlor.-ester blend.

TABLE VIII

Cylinder and Piston-ring Wear

	Amount of wear with chlor.-ester blend	*Amount of wear with mineral oil*	*% greater wear with mineral oil*
Buick test fleet—15,000 miles:			
Oil-ring wear, g.	0·1311	0·1795	37
Compression-ring wear, g.	0·1666	0·3692	121
Total ring wear, g.	0·2977	0·5487	84
Average cylinder wear, in.	0·00021	0·00029	38
Ford truck test fleet—12,500 miles:			
Oil-ring wear, g.	0·0753	0·1119	48
Compression-ring wear, g.	0·0791	0·1275	61
Total ring wear, g.	0·1544	0·2394	55
Average cylinder wear, in.	0·00018	0·00029	62
Chevrolet test fleet—30,000 miles:			
Oil-ring wear, g.	0·2621	0·4664	78
Compression-ring wear, g.	0·3522	0·3828	9
Total ring wear, g.	0·6143	0·8492	38
Average cylinder wear, in.	0·00019	0·00023	21

In all cases the cylinder wear is surprisingly low. All test runs were made at 50 m.p.h. under high-temperature conditions. There were relatively few starts and stops for mileage covered and, therefore, the low wear measured is added proof that corrosion under starting conditions is the cause of the major portion of cylinder wear. The cylinder-wear figures are the average of 6 measurements for each cylinder. The differences are small, but show that the average wear with the mineral oil is 40% greater than with the compounded oil.

Stability of Compounded Oil.

One of the most important factors in the selection of an addition agent is the question of its effect on the stability of the oil in which it is blended. Many products which are very desirable from the viewpoint of film strength, oiliness, low wear, &c., prove to be oxidation catalysts, and increase the rate of sludge and acid formation in the crankcase oil.

A desirable product should show either no catalytic action or a negative one. The amount of sludge formed during the 'beaker' corrosion test discussed above is a good preliminary test for this factor. Table IX gives the amount of sludge, in milligrams, produced per 10 g. of oil during the corrosion test. This indicates that high film-strength products may be powerful sludge-forming catalysts.

TABLE IX

Sludge Formation in Corrosion Test

Mineral oil with 1% of:	*Mg. per 10 g. of oil*	*Timken film strength (lb.)*
All mineral oils	none to 1·4	..
Methyldichlorostearate	none	28
Trichlororesorcinol	64	125
Triphenylchloromethane	27	74
Dichlorotetralin	43	95

There is no satisfactory laboratory method available to-day which will measure the relative stability of lubricants in terms of the actual changes they will undergo in service. The present available oxidation tests are of little practical value for this purpose, since they disregard the catalytic effect of the metals with which they will be in contact during service and the contamination from fuel, air, dust, cooling agents, &c. It is therefore necessary to depend upon actual tests on the road to study crankcase-oil service changes.

The results of the comparison of four oils in a Chevrolet test fleet are given in Table X. The test represents a total of 30,000 miles on each of 5 test cars. Runs of 1,100 miles were made between crankcase changes at an average speed of 50 m.p.h., over Oklahoma highways under July and August operating conditions. Oil no. 1 was a highly refined acid-treated Mid-Continent base oil; oil no. 2 was a solvent-treated Mid-Continent oil. Both oils were S.A.E.–20 grade. The characteristics of the fresh oil are given in the table.

The stability of the oils, as indicated by the Sligh and the Indiana oxidation-stability tests, indicate considerable superiority on the part of the solvent-treated oil. The Indiana tests indicate that the addition agent improves the stability of the acid-treated oil, and has little or no effect on the solvent-treated oil.

The actual service changes found in the road tests show: (1) that the wide differences found by the laboratory oxidation tests between solvent-treated and acid-treated oils do not occur in service; and (2) that the addition of the chlor.-ester tends to decrease rather than to increase the amount of oxidation of an oil in service.

It is essential that a crankcase lubricant does not produce corrosive decomposition products in service, and therefore the corrosiveness of the used crankcase oil is of value. The last section of Table X gives the average corrosion on copper and copper-lead for the four oils after 1,100 miles of service. Compared with Table V, it will be seen that there has been little change in this factor during use.

TABLE X

Crankcase-oil Stability in Service

	Mineral oil no. 1	*No. 1 plus chlor.-ester*	*Mineral oil no. 2*	*No. 2 plus chlor.-ester*
Fresh oil:				
Gravity	26·9	26·4	28·7	28·8
Flash-point	430	430	430	430
Fire-point	495	490	490	490
Viscosity at 100° F.	354	345	345	335
Viscosity at 210° F.	53·8	53·3	54·9	54·6
True colour	29	29	24	24
Neutralization no.	0·028	0·045	0·045	0·045
Carbon residue, %	0·25	0·25	0·13	0·12
Sligh no.	13	16	1·6	0·2
Indiana oxidation test:				
Hours to produce:				
100 mg. sludge per 10 g. of oil	38	45	99	96
1·0 neutralization no.	30	38	47	46
True-colour increase, 50 hr.	34	31	18	20
Chevrolet fleet runs:				
Average % sludge per 1,100-mile run	0·41	0·35	0·33	0·32
Average neutralization no. for 1,100-mile run	0·358	0·315	0·248	0·245
Average true colour	277	276	157	155
Corrosiveness of used crankcase oil:				
Milligrams loss per 100 sq. cm.				
Copper	4·8	2·7	11·7	13·9
Copper-lead	3·0	4·8	24·0	20·6

Oiliness

The greatly overworked word 'oiliness' has been used to cover a multitude of opinions and hypotheses on the theory of lubrication. We believe that, from its historical development, it should be limited to that phase of lubrication which considers the coefficient of friction under boundary and thin-film conditions. A low friction under all conditions of lubrication is desirable, but under boundary lubrication it is essential. This importance is not due to loss of power, but to the increased production of heat through high friction. The heat resulting from boundary lubrication with an oil of low oiliness may quickly result in temperatures so high that a mineral-oil film fails. A compounded oil may have oiliness without high load-carrying ability. This is characteristic of the fatty acids, which under thin-film conditions—but below their film strength—will show low friction and prevent failure by keeping the temperature at a safe point. The newer products, such as chlorinated esters, may have both oiliness and film strength—which permits the oiliness characteristics to function at higher loads and temperatures than in the case of the fatty acids.

It is probable that the characteristic of oiliness, as differentiated from film strength, is the result of the formation of a true adsorbed film of substantial thickness and permanence by polar molecules. Clark, Lincoln, and Sterrett, as well as many others, have shown that such films are unquestionably formed. It is therefore probable that the adsorbed film which gives oiliness is that which also gives metal protection against corrosion.

The relative oiliness value of two oils may be shown on any laboratory apparatus which will measure the resistance to motion of surfaces under thin-film conditions The relative values, however, may change widely—depending upon the conditions of test, metals used, &c.

For illustrative purposes a single example will be given. Fig. 5 shows the relationship between torque and load on an Almen machine, using a steel bushing and bronze pin at 1·2, 600, and 1,882 r.p.m. The results are shown for S.A.E.-30 mineral oil and for the same oil plus chlor.-ester. It is particularly interesting to note the decrease in load-carrying ability of the mineral oil with increased speed.

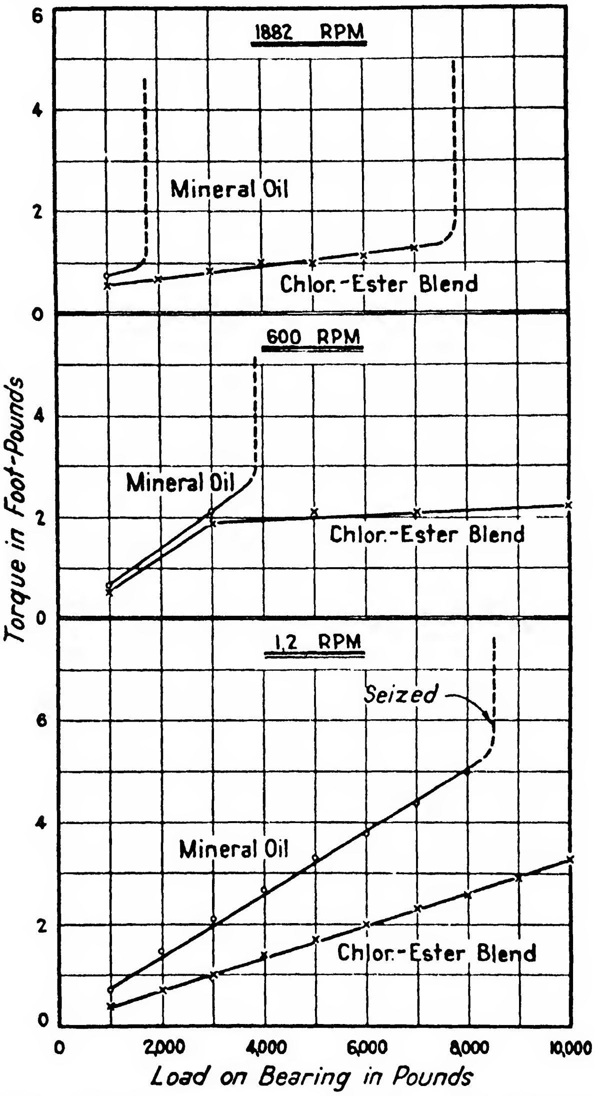


FIG. 5. Relation between Almen-machine torque, load, and speed with steel on bronze.

It is impossible in practical road tests to isolate the effects of oiliness as defined above; however, in all our road work we have found a definite lower operating temperature as measured by the differential increase in water temperature, temperature of oil from the bearings, and the oil-sump temperature for the blended oil as compared to the mineral oil under comparable operating conditions. As an example, in the Chevrolet fleet tests, where the comparisons were carried out under conditions as nearly identical as was physically possible, the average sump temperature of the cars on the chlor.-ester blend ran 8 to 10° F. below those on mineral oil.

Probably the best example we have of this characteristic was made at the Indianapolis speedway, where a Studebaker racing car was under test at 104 m.p.h. Switching from mineral oil to chlor.-ester blend and back showed an average lower sump temperature of 20° F. under identical driving conditions.

Miscellaneous Characteristics.

Consumption of Oil in Service. The best available information we have, both from dynamometer and road tests, indicates a decrease in consumption with the addition of chlor.-ester and similar oiliness agents, but the many factors entering into the consumption of crankcase oil make it difficult to isolate any one factor. In the Ford test fleet the blend showed an average mileage of 359·9 miles per qt. as compared to the mineral-oil average of 309, or an increase in mileage of 16%.

Under abnormally severe operating conditions much greater differences are found Thus, in the case of the Buick fleet during tests on Pikes Peak, the mineral oil showed a mileage per quart of only 237·5 as compared to the 403 for oil containing chlor.-ester. This large difference in consumption is partially due to different rates of wear during the 25,000 miles of operation.

Consumption of Addition Agent in Service. An addition agent may be consumed in service at a greater rate than the oil, due to either decomposition or vaporization. Such very volatile agents as pentachloroethane vaporize rapidly under high-temperature operating conditions—thus making them unsatisfactory for practical use, regardless of film strength.

Effect on Physical Characteristics of the Oil. In general, the small quantity of an addition agent has little or no effect on the physical characteristics of the oil, but a few factors must be considered in the final selection of a product. It should be perfectly soluble at all temperatures, so that neither the cloud nor the pour test of the oil is raised. The more volatile products may depress the flash-point, and volatile chlorinated hydrocarbons may give a peculiar bluish glow rather than a true flash. The material must not be water-soluble or tend to increase the emulsifying characteristics of the oil. As a rule the ester type of compound has low viscosity and a high viscosity index, but is used in too small a quantity to make an appreciable difference in the mineral oil.

Toxicity. Neither a compounding agent nor its decomposition products should have any toxic or obnoxious —such as odorous, anaesthetic, or corrosive—characteristics. The animal and vegetable oil bases cannot be used because of the offensive odour from the decomposition products of the fixed oil. Relatively volatile products, particularly highly chlorinated lighter hydrocarbons, are undesirable—both because of their loss through evaporation in service, and the possibility of harmful effects to the operator of a closed car.

Summary

The increased severity of the operating loads, speeds, and temperatures of the modern automotive engine have necessitated the improvement of crankcase oils. The true lubricating value or the ability to lubricate under severe or abnormal conditions may be improved by the use of a carefully selected addition agent. The selection of such an agent cannot be accomplished with a single or limited group of laboratory tests, but must ultimately depend upon actual service tests on the road. A detailed study in the laboratory of all the factors involved in lubrication is a valuable preliminary step. The various factors which must be studied are:

1. **Load-carrying Capacity,** which is the ability to carry the highest possible load at the highest probable temperature with a minimum supply of oil for an indefinite period.
2. **Oiliness,** which is the ability of a lubricant to operate under boundary or thin-film conditions with low friction and resultant low-heat formation.
3. **Metal Wear.** The oil must not only carry high loads with low friction, but must do so without appreciable metal wear.
4. **Corrosiveness.** Neither the agent nor its decomposition products should be corrosive to any metal with which it will come in contact during distribution or service.
5. **Corrosion Protection.** The product must not only be non-corrosive itself, but should form a strongly adsorbed film on metal surfaces which will protect them from the corrosive products of combustion and of oxidation of the mineral oil.
6. **Stability.** The addition agent must not only be stable under the highest temperatures reached, but it must not accelerate the oxidation of the mineral oil. It should act preferably as an inhibitor.
7. **Physical Characteristics.** Its physical characteristics, such as volatility, flash-point, pour test, solubility, &c., must not be detrimental to the required specifications of the mineral oil.
8. **Toxicity.** The addition agent must have neither toxic nor obnoxious characteristics.

Acknowledgement

The authors wish to acknowledge the assistance of Robert D. Best, in charge of the physical and mechanical testing laboratories, and of W. A. Jones, of the research staff of the Continental Oil Company, in the execution of this work.

REFERENCES

1. Boerlage, G. D., and Gravesteyn, B. J. J. Cylinder Wear in Diesel Engines. *Brit. Motorship*, **13** (150) (Aug. 1932).
2. Davis, L. L., and Best, R. D. Effect of Volatility on Oil Consumption. A.S.T.M., Detroit meeting (June 1935).
3. Dickinson, H. C., and Bridgeman, O. C. Fundamentals of Automotive Lubrication. *J.S.A.E.* **31** (1), 278–82 (1932).
4. Duff, W. N. Cylinder Wear. Report of the Inst. of Auto. Eng., *The Engineer*, 23 June and 30 June 1933.
5. Everett, H. A., and Stewart, F. C. Performance Tests of Lubricating Oils in Automotive Engines. *Penn. State Col. Eng. Sta. Bull.* no. 44.
6. Gatterman, Ludwig. *Laboratory Methods of Organic Chemistry*, translated from the 22nd German ed. (1932).
7. Heldt, P. M. Measurements show wear uniformly distributed around Cylinder Bore. *Auto. Ind.* **73** (3), 86–7 (1935). Distribution of Cylinder Wear. *Auto. Ind.* **73** (7), 205–6 (1935).
8. Keller, George H. Cylinder Wear measured by the Iron Content of Oil. *Auto. Ind.* 6 April, 1935.
9. Southcombe, J. E. Discussion of 'Oiliness and Lubrication', by R. M. Deeley, *Proc. Phys. Soc. London*, 28 Nov. 1919.
10. —— Germ-Process Theory. *Proc. Nat. Petr. Assoc.*, Spring meeting, Pittsburgh (1920).
11. Sparrow, S. W. Recent Developments on Main and Connecting-Rod Bearings. *J.S.A.E.* **35** (1), 229–37 (1934).
12. Teetor, M. O. The Influence of Engine Design on Oil Consumption. A.S.T.M., Detroit meeting (June 1935).
13. U.S.P. 1,319,129, issued 21 Oct. 1919. B.P. 130,877, issued 5 Feb. 1918. C.P. 196,215; Mexican P. 18,915.
14. U.S.P. 1,944,941, issued 30 Jan. 1934.
15. Wells, Henry M., and Southcombe, J. E. The Theory and Practice of Lubrication. *J.S.C.I.* (London), **39** (5), 51–60.
16. Wolf, H. R., and Mougey, H. C. Extreme-Pressure Lubricants. *Proc. A.P.I.* **13** (iii), 118–31 (1932).
17. Wooler, E. Observations on the Testing of Lubricants. *J.S.A.E.* **28** (1), 53–60 (1931).

MECHANICAL TESTING OF LUBRICANTS—LABORATORY ENGINES AND WORK FACTOR METHODS

By **G. M. MAVERICK, Sc.D., Manager, and A. J. BLACKWOOD, M.E., M.S.A.E.**
Bayway Development and Research, Standard Oil Development Company

THE testing of lubricants in automotive engines may logically be divided into two parts. First is the technique of conducting the test, including the selection of equipment best suited to produce the desired results and the proper selection and control of test conditions. To this should be added the means of evaluating the mechanical condition of the equipment both during and at the conclusion of the test. Second is the selection of the lubricant to be tested, and evaluation of the significance of changes in the mechanical condition of the equipment and physical and chemical changes which take place in the lubricant during the test, as related to the original properties of the lubricant. It is the first of these factors with which this article is concerned, namely, the methods employed to obtain the data rather than the interpretation of the data. Tests of the nature of those to be described are useful to the petroleum refiner and marketer who is desirous of improving lubricants with respect to performance characteristics; to the car manufacturer for determining how his car performs with various lubricants and who needs guidance in the setting of specifications; and to the consumer for the testing of different lubricants in his particular equipment.

Engine and other mechanical tests are intended to bring out one or more of the following performance characteristics of the lubricant used:

1. Consumption.
2. Sludging and oxidation (ring- and valve-sticking included).
3. Low-temperature performance.
4. Carbon formation.
5. Wear.

In the following, each of the above will be treated critically and a procedure outlined which it is felt offers the best hope for successful results by the investigator.

To begin with it should be recognized that the testing of lubricants in an internal-combustion engine is an extremely difficult art rather than an exact science. We are dealing with complex chemical materials, and the laws which govern their behaviour under the different operating conditions encountered are not well recognized. The range of operating conditions to be encountered in actual service is, for all practical purposes, infinite, and there is little assurance that the results of tests carried out under the most carefully controlled conditions will necessarily apply for approximately similar field conditions. Moreover, the internal-combustion engine is in itself a highly variable piece of machinery, changing almost from minute to minute in the way it performs. One might almost say that no two successive engine cycles exactly reproduce each other. Clearances change with use; the position of the piston rings are constantly shifting in the piston-ring grooves; scale in the cooling jackets changes the efficiency of heat transfer and varies the temperature differential for a given heat flow; carbon accumulation goes on at a variable rate, and the amount of oil reaching the cylinders varies as wear increases. Numerous other conditions are constantly changing, and all these serve to complicate the test results and make them difficult to reproduce.

Therefore, it is well for the research worker and the prospective investigator in this field to have clearly before him an appreciation of the difficulties of the problem. Few fixed rules can be set. It shall be our aim to describe methods of test which, according to our present concepts, offer the best possibilities of giving satisfactory results. While many of our readers will prefer their own test methods, none will deny that tests of lubricating properties must be carried out with scrupulous, painstaking, and intelligent exactitude if the results are to be trustworthy and reproducible.

Our first consideration becomes the selection of equipment for the tests. Generally speaking, there are two broad ways of approaching the problem. First, to test a large number of units, such as a commercial fleet, so that individual errors are minimized and representative results obtained on a basis of a group average. Second, to conduct all tests of a similar nature on one piece of equipment and take the necessary precautions to ensure the results being representative. Usually, the first method is too expensive for research work. While it would seem that fleet tests under variable conditions on a large number of units should give the most convincing results, actually it is practically an impossibility to conduct fleet tests and assemble data which are dependable and reproducible. For example, on the question of oil consumption, data for a fleet of 40 identical buses were analysed over one year's operation. For a single oil, consumption on individual buses varied as much as 85% from month to month, and the monthly fleet average varied as much as plus or minus 15% from the yearly average. With such changes obtaining on a single oil the difficulty of determining oil consumption on different oils can well be appreciated. Such uncertainty of results from fleet tests along with the general necessity of obtaining comparisons more rapidly than can be had by them, make questionable the fleet test as a satisfactory tool for lubricant research.

Tests on one piece of equipment offer more hope. Needless to say, where the cost permits and greater accuracy is required it is desirable to obtain check data on several pieces of equipment under controlled conditions. Unfortunately, lubricant tests are necessarily costly, and in the vast majority of cases the number of tests is limited by cost to one unit. For these reasons the discussion will be limited to methods of conducting tests on a single unit.

To obtain results of suitable precision it is necessary in practically all types of tests to use a reference lubricant as a basis of comparison. This reference product is run at regular intervals throughout a series of experiments, and the variation from test to test due to mechanical changes in the equipment can largely be accounted for by comparison of results with a reference line drawn through the reference oil data, as shown on Fig. 1.

Before a series of tests is started, then, a reference lubricant must be chosen. The considerations governing its selection depend upon the type of information desired and the equipment upon which the tests are to be made. Ordinarily a product is selected for the reference oil that is not perfect in respect to the characteristics to be studied —in order that the comparison with other lubricants may be expressed in relation to the reference oil. For example, if sludge formation is to be studied, it would be of no value to have as reference an oil which formed no sludge under the test conditions chosen, since such runs could not be rated in relation to those obtained on the oils being studied. Another characteristic of the reference oil which must be considered is viscosity. This must be selected to suit the engine.

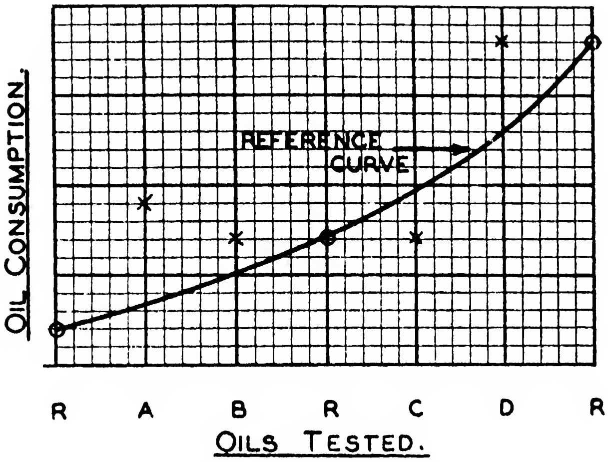


Fig. 1.

Having selected a reference oil, or a group of reference oils if the investigation is to cover a broad field of investigation on different grades of oils on different types of equipment, it is essential only to ensure that adequate supplies are made available, and that the total supply of each reference oil is well mixed before being stored in carefully sealed containers. There is no very exact knowledge as to how stable lubricants are when stored for long periods. Hence to minimize the possibility of changes occurring in a reference oil, careful consideration should be given to packing, storage temperature, and other details.

The five principal kinds of engine-lubricant tests will now be discussed, giving such details of equipment selection and test technique as it is felt will be of assistance to those interested in conducting experiments along these lines. It is hoped also that the information to be given will be of value to the reader in weeding out the good from the bad in the interpretation of so-called 'test results' which are currently being presented in support of claims for product performance.

I. Oil Consumption

Oil consumption is always a prime consideration in the evaluation of a lubricant for a given service. In a large percentage of cases consumption is the only criterion on which an oil is judged, particularly by the average passenger-car owner who in most instances has no other yardstick for the comparison of lubricants in his particular car. Consequently a superior lubricant must give low consumption as compared to other oils generally suitable for the specific service being considered.

Consumption of oil in actual road service is a composite of three quantities. First, there is the consumption of oil due to passage of lubricant past the piston rings into the combustion chamber where it is either burned or discharged with the engine exhaust; second, there is the consumption due to volatilization of the oil when subjected to heat and subsequent escape of the oil vapours through the crankcase breather or ventilator; and third, the consumption due to leakage at the gasketed joints, at the rear-main bearing, and at faulty oil-pipe connexions. The last cannot usually be attributed to oil characteristics although it is true that viscosity may influence the amount of leakage. In laboratory tests some leakage is inevitable, and since it is due to a mechanical fault, such leakage is collected and not considered as consumption.

Three types of oil-consumption tests are of interest. These are (*a*) torque-stand consumption tests, (*b*) road-consumption tests, and (*c*) dry sump oil-consumption tests. To this might be added the rear-wheel dynamometer consumption tests, but since few laboratories are equipped to conduct such tests and because the technique is essentially that of the road test, this method will not be described in great detail.

(*a*) Torque-stand Oil-consumption Tests.

Most laboratories will find the dynamometer test the most satisfactory method of running oil-consumption tests, since accurate control and reproduction of test conditions are possible. Furthermore, this test can in many cases be combined with and made a part of tests for carbon formation, sludge formation, engine wear, &c. The equipment needed consists of:

1. *The Engine*. Preferably a model in wide public use, and in good mechanical condition. Carburettor and ignition settings should conform to factory recommended practice.
2. *Power Absorption Unit*. Either an electric dynamometer (or generator) or water brake is satisfactory, the former lending itself more readily to automatic control if desired.
3. Accurate set of balances for weighing the oil charged to and drained from the engine.
4. *Temperature-measuring Instruments*. An electric potentiometer employing iron-constantan thermocouples is best adapted for this work.
5. Orsat or indicating exhaust-gas analyser for setting and adjusting the carburettor.
6. *Oil Cooler*. In many cases crankcase temperatures of an engine on a test-stand run above normal-road temperature, so that crankcase-temperature control is essential. Fans can be directed against the case, but this is not entirely satisfactory. Water sprays may be directed against the case, but if oil leakage occurs, as it frequently does, and since any leakage must be collected and accounted for, the spray system fails; water-jacketed crankcases may be built up, but these are cumbersome and expensive. The most satisfactory method is to employ a simple heat exchanger between the water-cooling system, or an external supply of cooling water, and the oil—and pump oil from the crankcase through the cooler and back to the crankcase by means of a small auxiliary gear pump driven by an electric motor. The crankcase oil temperature may be controlled by regulating either the rate of oil circulation or water feed to the cooler.
7. *Leakage Tray*. This is essential in oil-consumption tests, since some leakage is almost inevitable and must be

taken into consideration. The tray should be somewhat longer and wider than the engine, and about 2½ in. deep.

8. *Engine-cooling System.* A radiator and fan assembly may be used, but usually oversize units are needed to prevent boiling. A simple standpipe with overflow and cold-water make-up is the most convenient method. Of considerable convenience is an automatic device to actuate the cold-water valve for temperature control.

9. *Miscellaneous Equipment.* This should consist of a speed indicator, oil-pressure gauge, clock, manometers, thermocouples, or thermometers.

Consideration should be given to the following in selecting the operating conditions for the test:

1. *Cooling-water Temperature.* Normal temperatures are usually maintained thermostatically on the road at around 175–185° F. For cars without such control the temperature usually runs somewhat lower. A good operating temperature for test is 185° F.

2. *Crankcase Temperature.* Road tests have shown that for high-speed summer operation temperatures frequently reach 220–240° F. For heavy duty bus- and truck-engines 190–210° F. is more common, whereas for average passenger-car service 175–195° F. is normal. Winter operation will average only about 30° F. below these figures. Thus temperatures approximating to 195–205° F. will generally be satisfactory.

3. *Engine Speed.* Consumption increases rapidly with increased engine speed, doubling for each increase of 10 m.p.h. for most passenger cars, i.e. the consumption at 60 m.p.h. is about eight times the consumption at 30 m.p.h. If the test speed is too high, a difference in speed of 1 or 2 m.p.h. between comparative tests will account for more difference in oil consumption than may exist between the oils; if too low a speed is used consumption is low, and unless long tests are run the accuracy of measuring the consumption seriously affects results. While it is highly desirable to obtain consumption on each oil tested at various speeds, a single test does not readily lend itself to this. It is recommended that engine speed be set at a figure higher than that corresponding to average operating speeds on the road but well below maximum speeds. Few engines can operate at sustained maximum speeds for long periods without encountering mechanical troubles which tend to confuse the consumption results.

4. *Duration of Test.* While it is possible to obtain reasonably accurate consumption figures on a short test, the results are apt to be misleading when transposed to actual service results. Long-time results on an oil depend markedly upon the ring-sticking qualities of the oil, and the test should therefore be of sufficient duration to enable equilibrium engine conditions to obtain. Also, the test should be sufficiently long to overcome any initial volatility loss (for low flash-point oils particularly). Since some commercial operators run 2,000 miles between oil drainings, and since consumption over an equivalent period in the laboratory will best simulate road performance, it is recommended that a test of 50 hours' duration be made.

5. *Make-up Oil.* Here, again, customer practice should dictate when make-up oil is to be added. The test should start, of course, with the crankcase charge recommended by the car-engine manufacturer. The average driver adds oil when the level has dropped approximately 1 quart. During the test, therefore, make-up oil should be added whenever the oil level has dropped 1 quart. If crankcase oil-samples are desired during the run, to determine oil deterioration, such samples should be taken prior to the addition of oil, and an amount equivalent to the sample be replaced with the make-up oil. It is important that the total quantity of oil withdrawn as samples be kept as small as possible. The addition of the final make-up oil should occur such that at the end of the test, the level is down 1 quart below full charge.

6. *Operating Cycle.* Although not strictly necessary, it is highly desirable to run the test in cycles approximating the average type of service on the road, wherein normal driving is interspersed with periodic idling operation. Wherever possible, therefore, a cycle corresponding to say 9 minutes running and 1 minute idling should be adopted. The suggested load is approximately 20% above that necessary to operate on level road to compensate for accelerations, hill climbing, and the like.

Test Technique. The following test technique is given on the assumption that the foregoing considerations and recommendations have been adopted, and that the engine is perfectly clean throughout and in proper adjustment as to spark setting, carburettor adjustment, &c.

1. Check cooling system, thermocouples, battery, and place the leakage pan under the engine.

2. Add ½ crankcase charge (approximate) and start up engine. Make final adjustments wherever needed. Run until oil temperature is 150° F. Remove drain plug. When majority of oil has drained out, start engine and idle for 30 seconds. Stop and allow to drain until oil is dropping at a rate of 30 drops per minute. Replace drain plug. This procedure serves to give the 'zero oil level' point without which it is impossible to correct for the amount of oil which cannot be drained from the engine.

3. Weigh out the proper crankcase charge and put it into the crankcase. (Weigh container before and after adding oil to get the exact weight added to engine.)

4. Start engine and bring it gradually up to the operating conditions agreed upon.

5. Adjust water and oil temperatures to the desired values.

6. Complete test schedule.

7. After final shut-down of engine, allow oil to cool to 150° F. and drain as in 2 above.

8. Weigh the leakage oil (if any) accumulated in the pan. To do this accurately, pour as much of the oil as possible into a container of known tare weight. Weigh this oil. Now weigh several dry rags and with them mop up the remaining oil in the leakage pan and weigh the soaked rags. From the oil-weight data the actual consumption may be computed. (*Note.* It should be pointed out that all make-up oil is added to the engine by weight also.) From the specific gravity of the oil the volume consumption may be determined.

9. Dismantle engine. This includes removal of the pistons for cleaning, particularly in regard to any gummy or carbonaceous deposits in the piston-ring zone. At this point a complete engine inspection (see section II for method) may be made if desired, carbon deposits removed for weighing and chemical analysis, and wear measurements taken. Thoroughly spray out all engine parts with kerosine and blow dry.

10. Reassemble engine, taking particular care on piston-ring assembly to replace parts in the same position as removed. Engine parts should be oiled with the next lubricant to be tested before assembling.

11. Repeat procedure 1–10 for next oil on the programme.

(*b*) Road-consumption Tests.

In many cases, due to lack of laboratory engine-test facilities, road tests will be the only way by which consumption of different lubricants can be determined. Also, for those cases where laboratory tests are run, it is highly desirable to check the torque-stand results by operating cars on the road. The selection of a satisfactory route and driving schedule is the first consideration. The round-trip distance should be about 125 miles, thus eliminating the necessity of refuelling *en route*, and the adding of oil for cars having high oil consumption. Also, for consistent results, a driver should not be expected to drive much more than this distance at one stretch under the rigorous schedule necessary for such tests.

A rigid time-schedule should be laid out in advance by driving a car over the proposed route at the desired speed, and a time-table made showing where the car should be at intervals of not over 10 minutes. All stops should be specified. Where traffic signals are encountered, a stop must be scheduled whether or not the driver has the 'Go' signal. Drivers should be given the following instructions:

1. Adhere strictly to the time-schedule, making all scheduled stops.
2. Should time be lost at some point, make it up gradually, not by a burst of high speed.
3. Accelerate smoothly and use the brakes as little as safety permits.
4. Hold constant speed. Do not race the engine during idle.

Ordinarily road-consumption tests are made without overhauling the engine between tests other than to provide a routine check-up on spark plugs, ignition points, battery, chassis lubrication, tire pressures, cooling water, brakes, and steering mechanism. It is necessary, therefore, to run periodic tests—identical in all respects to the main tests—on a reference oil. Preferably, this should be every other test, although in an extended series it can be reduced to every third or fourth test. By this means mechanical changes and wear can be taken into consideration in evaluating final results. Each test should be a minimum of 500 miles for accurate consistent data. Beyond installation of a distance-type-indicating thermometer for the oil-sump temperature no special equipment is necessary for the car, although in many cases installation of extra distance-type-indicating thermometers may provide useful information. At the base garage there should be facilities for weighing oil accurately, for draining the crankcase, and for servicing the car. Assuming that the car has been put in good operating condition and that the crankcase has been flushed out, the principal points of operating technique are as follows:

1. Charge 1 gallon of test oil to crankcase. Drive car, or run engine in garage, until oil temperature is at 150° F. Check for oil leaks.

2. Place car on a level floor. It is desirable to mark the exact spot where the wheels rest and return the car to this exact mark on subsequent drains, thus ensuring a constant car position during the time the oil is being drained.

3. Remove drain plug and allow oil to run out. When main body of oil has drained, step on electric starter and crank engine for 30 seconds. Allow oil to drain until it reaches 30 drops per minute. Replace drain plug. This procedure serves to give the 'zero oil level' point without which it is impossible to correct for the amount of oil which cannot be drained from the engine.

4. Weigh out the proper crankcase charge and put it into the crankcase. (Weigh container before and after adding oil to get the exact amount added to the crankcase.)

5. Fill fuel tank, set milage indicator to zero miles, and start test.

6. After each round trip (125 miles), check oil level and add make-up where a full quart is necessary. Refuel.

7. It is desirable to allow the engine to cool down between each 125 or 250 miles of the test, corresponding to standing overnight. Whatever procedure is adopted in this respect should be adhered to throughout the series.

8. If different drivers are used, or if an extra observer is expected to make occasional trips, differences in weight carried may be compensated with sand-bags. Car windows should be shut (or open) to give uniform wind resistance from test to test.

9. At the end of the test (500 miles or more) return the car to the designated mark (2 above), allow the oil to cool to 150° F., and drain as in 3 above. Weigh drainings. Total consumption can then be calculated.

10. Check over and service car and repeat the above for the next oil.

11. If desired, fuel consumption can be recorded for each test. Draining the fuel tank at the start and finish for each test is more desirable than filling it full at the start and finish, due to the possibility of trapping air in one end of the tank in the full-tank method. (*Note.* If the car has an oil filter, it is desirable to remove it and by-pass the connexions for these tests, since usually it is impossible to drain the filter and also each test oil becomes partially contaminated with the preceding oil used.)

In running road-tests it is impossible to control road and atmospheric conditions. Hence, even though a reference oil is run frequently, there still exists variables to give erratic results. These may be largely overcome by running tests in pairs of cars, one car on the reference oil while the other is on a test oil, and reversing the oils in the cars at the end of each test. It should be pointed out that when running cars in pairs, the cars should not run close together on the road: at least 10 minutes should separate them. If run too close, the driver of the second car is under strain to 'keep-up' with the leader and does not drive normally.

For those laboratories having rear-wheel dynamometer facilities, tests combining the good features of both the road test and the controlled torque-stand tests can be planned from considerations of the above sections (*a*) and (*b*).

(*c*) Dry-sump Oil-consumption Tests.

For the well-equipped laboratory the method of test to be described in this section probably offers the best possibilities of examining the various factors which affect oil consumption. Operating an engine with a dry sump is not a new test method, in fact most aviation air-cooled engines normally run dry sump. But it has only been in recent years that the possibilities of adapting this type of operation to the study of the factors affecting oil consumption have been recognized.

Stewart and Risk published a preliminary report of their investigations of factors influencing oil consumption, using a dry-sump test set-up. Work on a similar set-up at the laboratories of the Standard Oil Development Company has shown that the possibilities and limitations of this type of test are as follows:

1. It offers a good method of determination of oil consumption as affected by

Engine conditions	*Physical oil characteristics*
Engine speed	Viscosity
Engine load	Viscosity index
Oil temperature	Gravity
Cooling water temp.	Boiling range
Rate of oil flow	Flash-point
Oil pressure	Volatility
Engine clearances	Crude source

2. The relative oil consumption of at least four different lubricants may be determined in one day's operation.
3. The tests are of short duration, so that mechanical changes in the engine from test to test do not seriously affect the results. Also, being of short duration, it is possible to run frequent reference oil tests without unduly increasing the costs.
4. The cost per test is low and the time required is not a serious drawback in planning an extensive series of tests.
5. It is possible to drain, flush, and change from one oil to another and back again without the necessity of stopping the engine or changing any of the conditions of operation.
6. Service consumption results cannot be predicted from these tests alone. An oil may show good consumption characteristics in this test and poor consumption in service due to chemical instability. If the oil sludges badly or causes piston-ring sticking, these will not be indicated in a short test but would seriously affect the long-time consumption results with that oil.
7. In a short test oil dilution from the fuel may give erroneous results. To overcome this it is advisable to use a very volatile fuel set to run with a lean mixture and at moderately high-engine temperature. If available, it is preferable to use a gaseous fuel to eliminate dilution.
8. Oil pressure, oil-flow rate, and oil temperature can be controlled independently of engine speed and load.
9. Results must be interpreted with due respect to the fact that the initial consumption may be due to the loss of low-boiling fractions.

It is apparent from the above that while this test of itself may not give a true index of the oil-consumption qualities of a lubricant, it is a valuable tool in establishing the effect of physical factors on oil consumption and if coincidental tests are run for chemical stability, the combination of the two tells a fairly reliable story in so far as predicting ultimate service performance.

Fig. 2 is a photograph of such a dry-sump installation. The engine must be selected, or slightly rebuilt, to ensure that all oil draining into the crankcase runs freely down to the crankcase outlet. At the outlet the oil is picked up by a scavenging pump, separately driven by an electric motor, and delivered to the oil container on one of the end pair of scales. These scales can be read to 1/1,000 lb. and are equipped with suitable dashpots. The containers on the scale are provided with steam coils and electric heaters suspended in the oil to control oil temperature. A delivery pump, separately driven by a variable speed electric motor, picks up oil from the container on the scales and delivers it via the distributing oil line to the engine. In the delivery line to the engine are a calibrated Venturi meter for measuring rate of oil flow and a pressure gauge. The pressure-relief valve is removed from the engine, so that all oil delivered to the engine oil-line flows to the bearings and is not by-passed to the crankcase.

In operation the engine is first brought up to the desired load, speed, and temperature, after which the oil system is adjusted to the requisite temperature, pressure, and flow rate. Readings on the oil-weight scale are then read at 5-minute intervals over a period of 1 hour, and plotted on time-weight coordinates. The slope of the readings gives the rate of oil consumption. Typical consumption results from such a test are shown in Fig. 3.

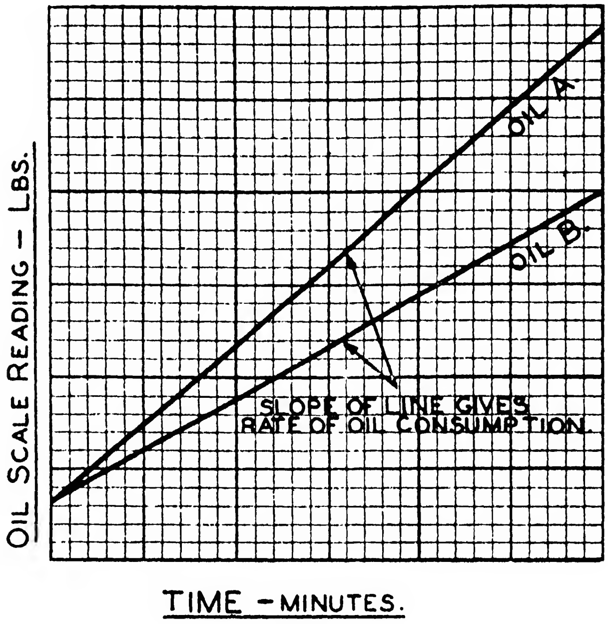


Fig. 3.

To change to another oil the lubricant is first preheated to the desired temperature in the container on the second of the two scales. Oil from the engine is then directed into one side of the middle container which is partitioned into two halves. When the original container is almost empty, the valve from the other half of the middle container is cut in and the engine flushed. The engine is then again drained into the first section of the middle container and finally swung over on to the next test oil. The flushing is, of course, done with the oil to be tested next. A four-way valve on the lines from the three containers to the engine, and a swivel pipe above the containers to direct oil from the engine into any of the three, makes the above change-over a simple matter and accomplishable without stopping the engine.

II. Sludging and Oxidation

Without any doubt the word 'sludge' has become the most loosely used word in the vocabulary of those members of the petroleum and automotive fraternities who are concerned with performance characteristics of lubricants. It has been used to describe any and all irregularities in the appearance of an engine outside of the combustion chamber proper, as well as the visual appearance and consistency of the used oil drained from an engine. Actually the precise definition of sludge is of little importance. Whether or not a deposit of material in the crankcase is sludge in the technical interpretation of the term, or simply a mixture of oil and carbon particles, the reputation of the oil used suffers equally in the eyes of the owner or operator or mechanic, since his judgement must necessarily be guided by appearance alone.

Broadly speaking, therefore, we can define sludge forma-

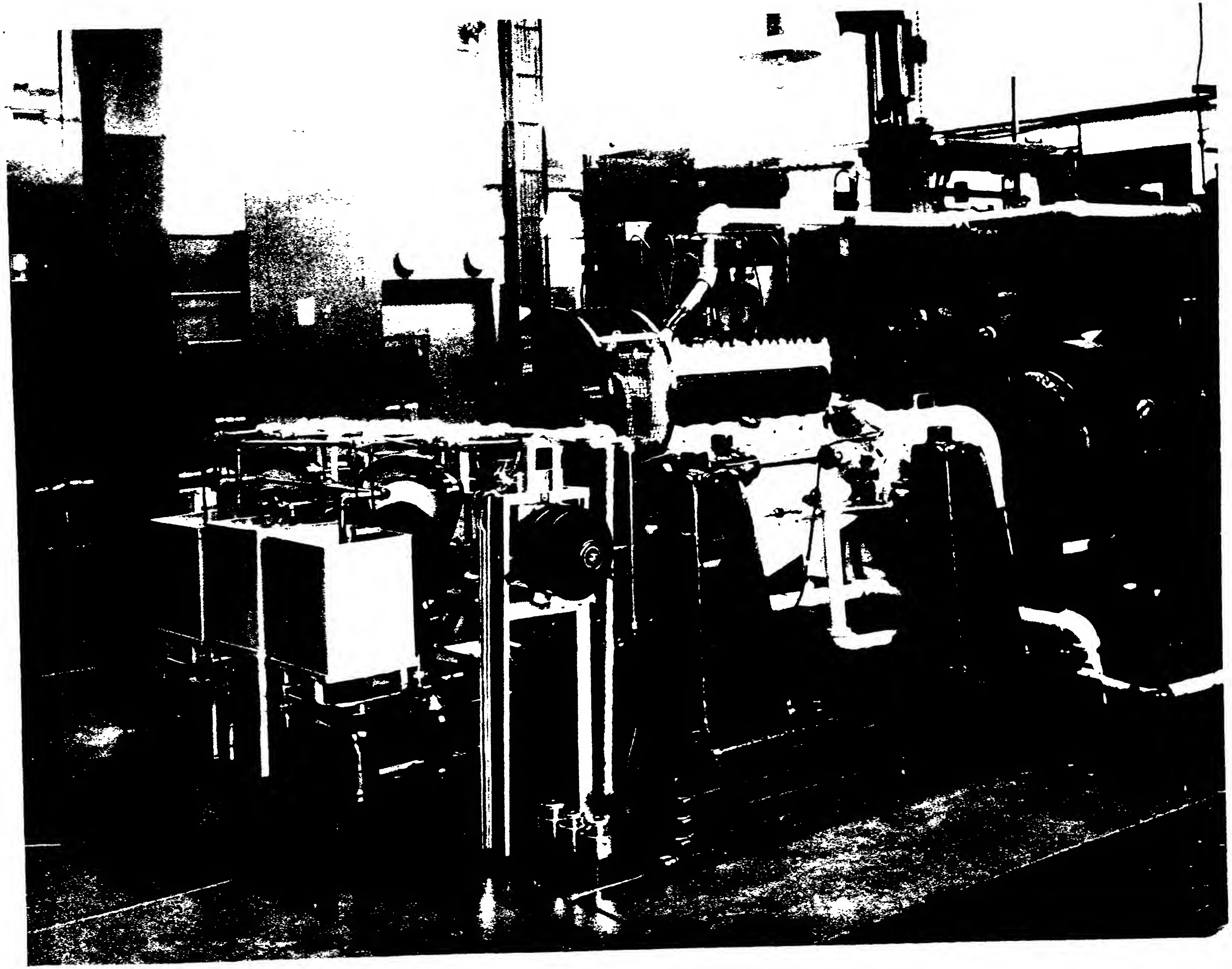


FIG. 2. Dry sump oil consumption apparatus, Standard Oil Development Company

tion as being one of, or a combination of two or more of, the following:

(*a*) The accumulation of solid carbonaceous material in the bottom of the crankcase. This material resembles 'coffee grounds' and may include varying amounts of a somewhat thick asphaltic material.

(*b*) The accumulation in various parts of the engine, particularly in valve chambers, flywheel housings, rocker-arm covers, oil screen, and crankcase, of a semi-solid material of smooth texture resembling black cold cream.

(*c*) The suspension in the oil of minute solid particles of oxidized material which gradually thicken the oil and centrifuge out in hollow shafts and bearings, and, in extreme cases, clog the oil lines. The particles settle out of some oils on standing and in others stay almost entirely suspended in the oil.

(*d*) Caking on the undersides of pistons, crank-throws, connecting-rods, and sundry other parts with a carbonaceous material closely resembling the carbon accumulation in the combustion chamber.

(*e*) The accumulation of deposits in the piston-ring grooves in the piston oil-ring slits and ring-groove drain-holes.

There are many theories which have been advanced to explain why lubricants sludge and many oils have been marketed claiming non-sludging characteristics. The truth of the matter is that while some oils are undoubtedly vastly superior to others, the exact reason for their being so is not yet clearly understood despite the many theories advanced. It still remains a matter of testing the finished products in actual engines and in service before it can definitely be stated that a given lubricant has superior non-sludging characteristics. There is as yet no widely accepted laboratory test which can be employed to precisely predict this quality of a lubricant. Blow-by past the piston-rings may include products of incomplete combustion which are good emulsifiers. These emulsifying materials may, even with good lubricants, overshadow degradation products of oil, particularly in cold weather.

The 'cold cream' or emulsion type of sludge is not generally regarded seriously by the petroleum technologist, since water must be present, along with solid material in the oil, to produce this type of sludge. Furthermore, it is rare that accumulations of this type even in relatively large quantities result in damage to the engine. Only occasionally will the emulsion collect on the wire screen at the pump inlet and, if the mesh is small, ultimately stop the flow of oil. This type of emulsion sludge may be serious in cold weather where the moisture particles freeze into small ice crystals and clog the oil screen within a few minutes after starting. The water may accumulate in consequence of a leaky cylinder-head gasket, a cracked casting, or, what is usually the case, a badly worn engine which permits combustion products of high moisture content (10–12%) to leak past piston-rings or exhaust-valve guides. When these products come in contact with surfaces at a temperature below about 130° F., moisture will condense. Consequently, the common emulsion sludge cannot be entirely overcome in a worn engine operating at relatively low temperature even with the best of lubricants.

Engine tests for sludging characteristics of lubricants are difficult to conduct successfully. Probably no engine test gives more difficulty than one aimed at evaluating the sludging characteristics of an oil. That some oils sludge more than others in service cannot be questioned, but it is a most difficult task to reproduce this in the laboratory. Experience has indicated that such tests may best be carried out in a heavy-duty engine, preferably overhead valve design, operated in cycles approximating to the service encountered in the field. This cyclic operation is much more effective than continuous steady load and speed running, since the alternate heating and cooling apparently has a marked effect on sludge formation. Road tests of individual cars, and fleet tests, even though under controlled conditions, are not recommended, due to the length of time required to obtain results. In the final analysis, however, service tests should be run before placing the final stamp of approval on a product.

There is considerable leeway in the selection of equipment and test technique desired for running engine-sludge tests in the laboratory. The following procedure is recommended on the strength of having given good results over an extended period of time.

1. **Test Equipment.** Engine—preferably a heavy-duty valve-in-head engine. Reliability and ruggedness are essential if a long programme is contemplated. The engine fan should be connected so as to direct cool air over the engine, particularly for cooling valve covers, carburettors, &c.

Carburettor control—an automatic system of cams, relays, timer, and solenoid may be provided periodically to open and close the throttle to give the desired cyclic operation. It is also desirable to provide an electric heater for the carburettor air with thermostatic control.

The remainder of the test equipment is substantially that outlined previously for conducting laboratory oil-consumption tests.

2. **Operating Conditions.**

Engine speeds, 400 (idle) to governed speed (say 2,000 r.p.m.).
Engine loads, idle to ¾ full torque.
Oil temperature, 200–220° F.
Water temperature, 180–190° F.
Carburettor and spark, factory recommended settings.
Carburettor air inlet, 100° F.

3. **Test Technique** (assume clean engine ready to start test).

(*a*) In charging the oil to the engine it is desirable to follow the procedure outlined under the laboratory test for oil consumption so that an accurate record of consumption may be made.

(*b*) Start engine and adjust all controls to desired values. Let engine run for a period of 75–100 hours.

(*c*) Samples of crankcase oil should be obtained approximately every 10 hours for analysis. Samples should not be taken immediately after adding make-up oil. Make-up should be added when crankcase level drops to the ⅔ full mark or at definite time intervals.

(*d*) At the end of the test proceed as follows:

1. Drain oil and submit to analytical laboratory for complete inspection.

2. Take engine completely apart, including pistons, rings, and valves.

3. Carefully inspect each individual valve, piston, piston-ring, bearing, cylinder, combustion chamber, valve chamber, crankcase, oil screen, crankshaft, &c. Each part examined may be given a numerical rating (the 0–10 basis is satisfactory) by an experienced man, and a composite numerical value of general engine condition determined.

Special emphasis can be given certain parts as desired. Fig. 4 is a suggested engine inspection sheet which has been found to be very convenient for checking off the condition of the individual parts being inspected. Numerical ratings can be established on any desired basis. In addition a short summary of any unusual conditions noted should be included.

4. Remove carbon for weighing. It is desirable to keep piston top, cylinder surface, and cylinder-head carbons separately for correlation against surface temperature. In other words, this test may be used as part of any carbon accumulation programme.

5. Remove deposits in and around piston-rings and grooves for weighing and analysis.

6. Remove any accumulated crankcase-sludge deposits for analysis.

7. Carefully clean all engine parts, not omitting undersides of pistons and crankshaft, and reassemble. Grind valves. Check bearings, rings, &c., for broken or defective parts before reassembling. Use new spark plugs on each test.

8. Thoroughly spray all parts with kerosine or similar material. Follow this by spraying with the next oil to be tested.

9. Reassemble for next test.

In conducting these experiments it is necessary to adopt the 'reference oil' method described in the introductory paragraphs, and to make the comparisons between lubricants with respect to the results on the periodic reference oil tests.

Ring Sticking.

The problem of piston-ring sticking is essentially one encountered at high-operating temperatures, and for this reason is most prevalent in high-duty aviation engines and occasionally in heavy-duty bus and truck operation. It is not uncommon in Diesel-engine operation but is rarely found in Otto-cycle marine engines and low-compression automobile engines. It is particularly serious in aviation service, since under severe service, when a piston-ring sticks, blow-by occurs and as a result the piston itself frequently burns out, resulting in a forced landing. Consequently the rapid strides made in specific output of aviation engines in recent years has greatly increased the necessity for lubricants of outstanding ability to minimize piston-ring sticking, and at present this question of ring sticking is without doubt the most important single lubricating problem affecting the future development of the aviation engine. Moreover, higher output automobile engines and the high output, high-speed Diesel engines are also offering a problem in preventing ring sticking which will be of increasing importance as specific output increases.

As in the case of sludge formation, ring sticking is difficult to determine by any of the known laboratory tests, and again engine tests must be used in the final analysis. For this work it has been found that single-cylinder engines operating at high temperature offer the best type of test for ring sticking, since such tests are fairly economical to conduct and, if properly run, are reproducible.

III. Low-temperature Performance

The performance of lubricants in winter weather is becoming increasingly important each year. Highway facilities for keeping roads open in the worst of winter weather has greatly increased the passenger car, bus, and truck operation in cold weather. Commercial air lines now operate the year round. Industrial and agricultural tractors are rapidly increasing in number and face a problem in cold-weather starting. The recent trend of the railroads to increase their automotive equipment will bring them problems in cold-weather operation. Perhaps no better evidence of the importance of the cold-weather performance of lubricants can be presented than to point out the unusual activity of the American Automotive Engineering societies in sponsoring the special classification and designation of oils for low temperature use.

There are two major problems involved in the low-temperature performance of lubricants in engines, namely, cold starting and oil pumping. The cold-starting problem involves the two considerations of power or torque required to crank the engine with different lubricants and the wear which occurs during the cold-starting operation. Oil pumping involves the determination of the lowest temperature at which various lubricants may be pumped to the working parts of the engine and the quantity pumped at different temperatures.

The laws governing the torque required to crank engines as a function of viscosity, and the pumping characteristics of lubricants as a function of viscosity and pour-point, are so well recognized as a result of investigations carried out during the past few years that great detail is not warranted in describing methods of conducting such tests. The attached bibliography lists several references covering these phases of lubricant performance. However, the necessity of investigating some closely related problem frequently arises, and for this reason the general technique is given below. Such related problems might include wear and torques for various bearing materials, pistons, and cylinders; the effect of various compounding materials in the oil and the like.

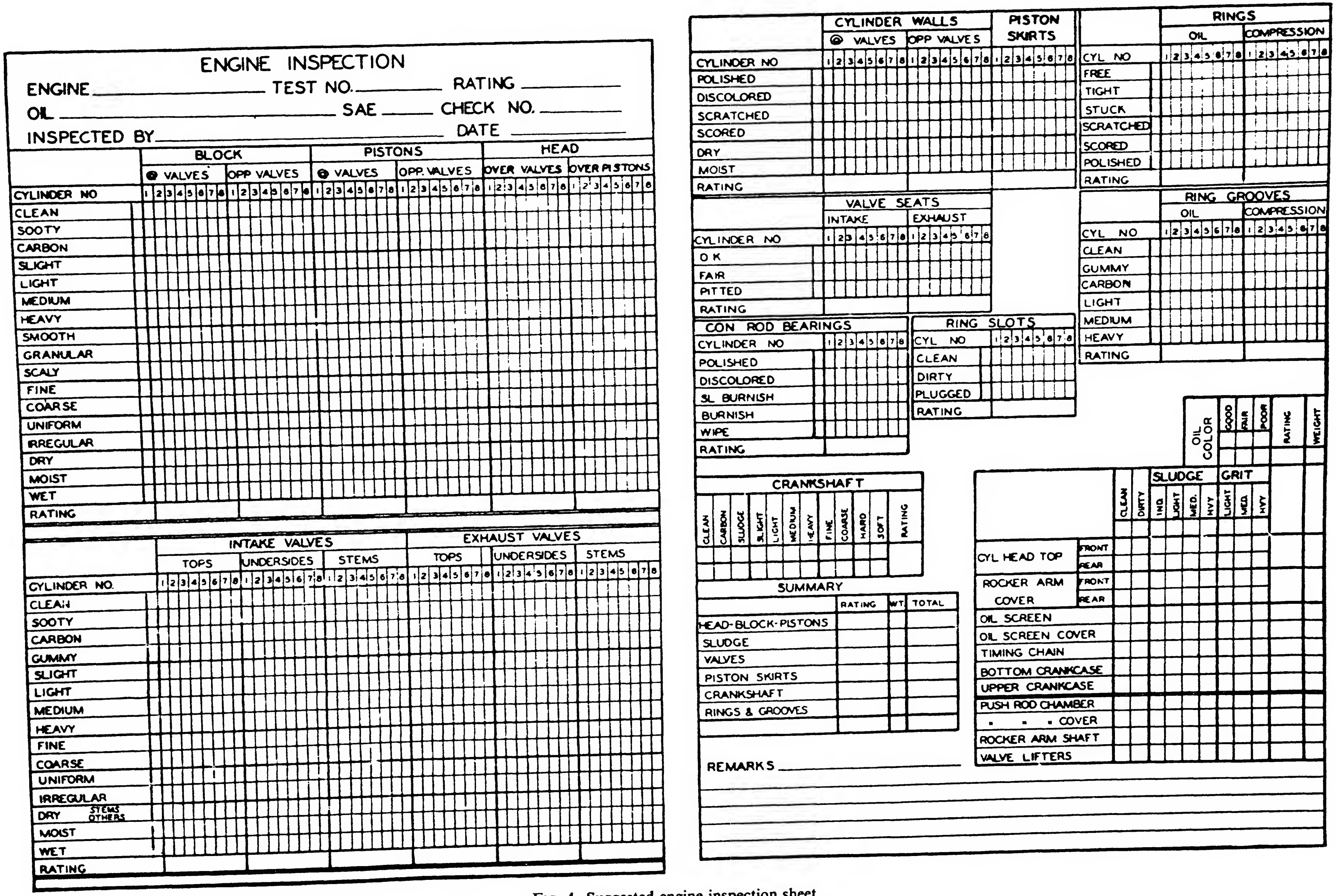
Cold-starting Tests

These may be divided into two types, the dynamometer test and the car test. The dynamometer test is particularly well suited to tests involving torque measurements, and the car tests are advisable for determining maximum permissible viscosity for starting various cars as dependent upon engine, starting equipment, battery condition, &c.

(*a*) **Dynamometer Tests.** The engine may be 'cranked' by a dynamometer and torques determined at various speeds from 'breakaway' to say 150 r.p.m.; or a constant speed electric motor may be used to drive the engine at some constant speed (preferably about 40 r.p.m., which is near the limiting lower speed which will permit starting a car) through a suitable gear-box, and torque requirements determined either electrically by meters on the power line, or by cradling the motor and gear-box and recording the reaction torque. The dynamometer is the more common method used, and the following technique is recommended:

(1) Warm up the engine on the test oil until the crankcase temperature reaches 150° F. and the water-jacket temperature 165° F. These are average winter-operating temperatures.

(2) Shut off the fuel supply and let carburettor run dry. Some investigators prefer to have a charge of preheated oil ready at this point, and drain the crankcase to remove possible dilution, replacing with the heated oil. Then the engine is motored over (with dry carburettor) by the dynamometer to get this fresh oil well distributed throughout the engine.



ENGINE INSPECTION

ENGINE ______ TEST NO. ______ RATING ______

OIL ______ SAE ______ CHECK NO. ______

INSPECTED BY ______ DATE ______

	BLOCK		PISTONS		HEAD	
	@ VALVES	OPP VALVES	@ VALVES	OPP. VALVES	OVER VALVES	OVER PISTONS
CYLINDER NO	1 2 3 4 5 6 7 8	1 2 3 4 5 6 7 8	1 2 3 4 5 6 7 8	1 2 3 4 5 6 7 8	1 2 3 4 5 6 7 8	1 2 3 4 5 6 7 8
CLEAN						
SOOTY						
CARBON						
SLIGHT						
LIGHT						
MEDIUM						
HEAVY						
SMOOTH						
GRANULAR						
SCALY						
FINE						
COARSE						
UNIFORM						
IRREGULAR						
DRY						
MOIST						
WET						
RATING						

	INTAKE VALVES			EXHAUST VALVES		
	TOPS	UNDERSIDES	STEMS	TOPS	UNDERSIDES	STEMS
CYLINDER NO.	1 2 3 4 5 6 7 8	1 2 3 4 5 6 7 8	1 2 3 4 5 6 7 8	1 2 3 4 5 6 7 8	1 2 3 4 5 6 7 8	1 2 3 4 5 6 7 8
CLEAN						
SOOTY						
CARBON						
GUMMY						
SLIGHT						
LIGHT						
MEDIUM						
HEAVY						
FINE						
COARSE						
UNIFORM						
IRREGULAR						
DRY STEMS OTHERS						
MOIST						
WET						
RATING						

	CYLINDER WALLS		PISTON SKIRTS
	@ VALVES	OPP VALVES	
CYLINDER NO	1 2 3 4 5 6 7 8	1 2 3 4 5 6 7 8	1 2 3 4 5 6 7 8
POLISHED			
DISCOLORED			
SCRATCHED			
SCORED			
DRY			
MOIST			
RATING			

	RINGS	
	OIL	COMPRESSION
CYL NO	1 2 3 4 5 6 7 8	1 2 3 4 5 6 7 8
FREE		
TIGHT		
STUCK		
SCRATCHED		
SCORED		
POLISHED		
RATING		

	VALVE SEATS	
	INTAKE	EXHAUST
CYLINDER NO	1 2 3 4 5 6 7 8	1 2 3 4 5 6 7 8
O K		
FAIR		
PITTED		
RATING		

	RING GROOVES	
	OIL	COMPRESSION
CYL NO	1 2 3 4 5 6 7 8	1 2 3 4 5 6 7 8
CLEAN		
GUMMY		
CARBON		
LIGHT		
MEDIUM		
HEAVY		
RATING		

CON ROD BEARINGS	
CYLINDER NO	1 2 3 4 5 6 7 8
POLISHED	
DISCOLORED	
SL BURNISH	
BURNISH	
WIPE	
RATING	

RING SLOTS	
CYL NO	1 2 3 4 5 6 7 8
CLEAN	
DIRTY	
PLUGGED	
RATING	

CRANKSHAFT

CLEAN	CARBON	SLUDGE	SLIGHT	LIGHT	MEDIUM	HEAVY	FINE	COARSE	HARD	SOFT	RATING

SUMMARY

	RATING	WT.	TOTAL
HEAD-BLOCK-PISTONS			
SLUDGE			
VALVES			
PISTON SKIRTS			
CRANKSHAFT			
RINGS & GROOVES			

OIL COLOR	GOOD	FAIR	POOR	RATING	WEIGHT

		CLEAN	DIRTY	SLUDGE IND.	SLUDGE LIGHT	SLUDGE MED.	SLUDGE HVY	GRIT LIGHT	GRIT MED.	GRIT HVY
CYL HEAD TOP	FRONT									
	REAR									
ROCKER ARM COVER	FRONT									
	REAR									
OIL SCREEN										
OIL SCREEN COVER										
TIMING CHAIN										
BOTTOM CRANKCASE										
UPPER CRANKCASE										
PUSH ROD CHAMBER										
" " COVER										
ROCKER ARM SHAFT										
VALVE LIFTERS										

REMARKS ______

FIG. 4. Suggested engine inspection sheet.

(3) Allow engine to cool to the desired temperature and remain at this temperature for at least 2 hours to 'soak'. Thermocouples or thermometers in the crankcase at two or three locations and in the water-jackets should all check within one degree before starting the actual test. A constant-temperature cold room is a prerequisite for this type of test.

(4) Determine 'breakaway' torque either by gradually increasing dynamometer torque or by a supplementary dead-weight system using a pulley and shot bucket on the shaft.

(5) Slowly increase speed in small increments and record torque at each step until a speed of 150 r.p.m. is reached. This entire procedure should not exceed 10 minutes, since work is being done during the motoring operation and this heats up the oil.

(6) Start engine firing and again warm up to conditions enumerated in (1). Follow the above steps for the next succeeding test.

It has been found that various temperatures may be investigated on one oil without the necessity of warming up between runs, and with extremely little variation in the torque required by the two methods. If wear measurements for a series of starts are desired, then the warming-up step should by all means be included, since cold-starting wear occurs during the warm-up period as well as during the starting operation proper.

(*b*) **Car Tests.** Although a great deal is known about the general problem of starting car engines in cold weather, the continued improvement in starting-system design, the introduction of new piston, cylinder, and bearing materials, improvements in piston-rings, improvement in carburettors, and improved fuels and lubricants all tend to make this a continually changing problem. Since it is changing it will necessarily be a subject of study for some time to come.

The test technique is relatively simple although there are a few points of considerable importance to be kept in mind in conducting the tests. The first is the battery. For truly comparative results the battery must be in the same condition for each test. Since the drain on the battery is high during low-temperature cranking and consequently its charge life rapidly diminishing, it is advisable to have available several identical (and preferably new) batteries with outside connexions to permit of changing batteries for each test. Between tests the used batteries should be recharged to a given specific gravity of the electrolyte. Extreme care must be exercised to ensure that during a test the connexions are all clean and tight and the outside leads must be of ample size to guarantee a low-resistance drop. Also since most batteries are well insulated thermally, it is necessary to keep the battery to be used on a given test at the test temperature for several hours prior to use. This is of considerable importance, due to the change in battery efficiency with temperature. Naturally a starting test should include the battery, inasmuch as its output largely determines the cranking speed under a given set of conditions. For best results a single battery should not be used more than a total of one minute at low temperature without recharging.

Next is the measuring of cranking speed. While revolution counters may be connected, this is usually difficult due to the fact that cars vary so widely in design. The easiest method is to remove the distributor cap and watch the rotor. By using a stop-watch and recording the time for a few complete revolutions when the starter button is depressed, the cranking speed may be calculated rather closely.

The actual testing should probably best be done in two separate steps. The first is to determine the lowest cranking speed which will permit the given car to start. This is a matter of lifting fuel from the carburettor and delivering it to the cylinders. To minimize the effect of fuel characteristics this speed might best be obtained at relatively high temperatures. To accomplish this oils of increasing viscosity should be run at say 25° F. until the cranking speed at that temperature is reduced to a point where, with the normal procedure of choking and throttle manipulation, it is impossible to start the engine. A suggested procedure for the above is as follows:

(*a*) Make sure electrical system and carburettor system are in perfect condition. Particularly make sure that the choke or strangler operates properly and neither refuses to close fully when applied nor open fully when released.

(*b*) Drain, flush, and charge crankcase with the oil to be used.

(*c*) Warm up engine. Do not run longer than necessary so that oil will not become diluted with fuel.

(*d*) Shut off fuel (valve in line) and drain carburettor.

(*e*) Cool test room to desired (25° F.) temperature and allow to 'soak' for a minimum of 3 hours.

(*f*) Remove distributor cap and determine cranking speed as outlined above.

(*g*) Replace cap and turn on fuel.

(*h*) Attempt to start car.

(*i*) Repeat with oils of increasing viscosity until cranking speed is so low that starting cannot be attained.

This minimum cranking speed is essentially constant for a given fuel system. Since the actual cranking speed varies with battery efficiency, oil viscosity, and engine-design features, it now becomes necessary to determine the limiting oil viscosity to give the required minimum speed at various temperatures. To attain these data the following additional procedure is recommended:

(*a*) Follow above steps *a*–*f* for the first oil to be tested, preferably a fairly viscous oil (S.A.E. 30 grade).

(*b*) Lower temperature in 10° F. steps and determine cranking speed for each temperature until the cranking speed falls below the required minimum.

(*c*) Repeat the above two steps for oils of S.A.E. 20, 20-W, and 10-W grade. If desired, predilute with kerosine to a known viscosity.

(*c*) **Oil Pumping.** The pumping characteristics of an oil are, surprisingly enough, rather difficult to measure. This may be realized from consideration of the following items:

(*a*) In an actual engine the use of the choke during starting and warming up may cause so much liquid fuel to reach the crankcase that the oil pump may actually be delivering to the bearings during the first few minutes of operation a heavily diluted mixture of oil and fuel.

(*b*) Engines which have excessive blow-by, even though liquid fuel may not reach the crankcase in excessive amounts, may heat up the oil very quickly and permit even a 'solid' oil to pump in a relatively short period.

(*c*) Oil pressure is not indicative of the oil flow, since for a given pressure the relative amount reaching the bearings and being bypassed at the pressure-relief valve is indeterminate. Tight bearings will increase the bypass quantity, and loose bearings will do the opposite. One loose bearing may result in the remainder being starved.

A simulated bench test, involving a crankcase and pump (externally driven) and an oil-delivery line with restricted outlets corresponding to the bearings offers the best possibilities of investigating pumping characteristics. Cooling can be attained by a suitable dry ice and alcohol bath surrounding the crankcase. Even this arrangement cannot be operated on a continuous circulating basis, since at low temperatures the heat transfer is poor and the main body of the oil is not agitated, resulting in wide-temperature differentials between the sump and the pump lines. Also the pump work tends to heat up the oil rapidly.

However, by allowing the entire system to reach successively lower equilibrium temperatures and at each temperature to start the pump for a period sufficiently long to measure pressures and oil delivery to the line outlets, and to observe channelling or cavitation at the pump, considerable useful information on lubricants can be obtained and the effect of pump design, screen size, and the like may be studied.

IV. Carbon Formation

It has been previously stated that the average motorist measures oil quality largely on a basis of oil consumption. Ten years ago this was not the case, since average driving speeds were appreciably lower and high oil-consumption was not as prevalent. In those earlier days an oil was more apt to be judged by the frequency with which a 'valve and carbon' job was required, and while it was true that the valve materials were primarily responsible for the frequency of such maintainance, at the same time it offered relatively frequent opportunities to observe the amount of carbon which had accumulated, and as a result oils were judged by the amount of carbon formed. To-day valve materials have so greatly improved that frequently passenger cars operate practically their entire life without the necessity of grinding valves. In the same interim, compression pressures have increased markedly. These developments have necessitated better oils in so far as carbon formation is concerned for two reasons. First, the carbon is removed less frequently due to longer valve life and it does not accumulate in large quantities over long distances. Second, carbon deposits will increase the tendency to detonate. As a matter of fact, the driver of to-day usually is aware of carbon in the engine only by the increased tendency to detonate, and the oils are frequently judged by the distance which can be travelled before the spark must be retarded to eliminate knock, or a change to a higher octane number fuel is required. So while consumption has superseded carbon-forming tendency as the nominal yardstick for judging oils, at the same time the tendency of oils to form carbon are readily observed and is still a matter of serious importance, particularly in cases where oil consumption is high and carbon deposition correspondingly great.

If there exists a set of laws governing the carbon-forming characteristics of lubricants, then it can be stated that either these laws are not yet well understood or that the number of variables entering into the question of carbon formation are too complicated to permit establishing a definite rational method of predicting the results. For one thing, the particular fuels used by two consumers having the same brand lubricant in the same kind of equipment and running under the same operating conditions may result in carbon formation differing several fold in quantity and in the nature of the deposit. This factor has not been well recognized in the past and is only partially understood at present. Fuel volatility, anti-knock value in relation to the engine requirements, and the use of blended (benzol, alcohol, &c.) fuels play important roles. There are fuels on the market containing oils which in some cases increase carbon formation while others of more merit effectively diminish the accumulation of hard adhesive carbon deposits. It is obvious that the same fuel must be used in all tests.

The actual testing in engines to determine the carbon-forming tendencies of lubricants thus presents a difficult problem. If conducted under one set of conditions, the results obtained may be entirely misleading for another set of conditions, and service results may disagree with both. Nevertheless, such tests are of considerable value since in general relative results obtained under similar conditions are usually indicative of relative service performance regardless of the many exceptions.

Since this problem is so involved, no definite recommendations can be made which will ensure positive comparative results. The following suggestions are offered simply as a guide for those interested in seeking additional engine-test data on this problem:

1. Use a normal fuel approximating in its characteristics to the fuel which will be used by the average consumer of the particular oils to be studied.
2. Select operating conditions conducive to high carbon formation. This obtains on most engines at part load and moderate engine speed.
3. Operate on a cyclic basis including periodic full throttle and/or high speed. An oil which forms large quantities of carbon at light load should not be unduly penalized since this carbon may fluff or burn off under more severe operation. Cyclic operation will tend to give more nearly representative results.
4. Use a fixed reference oil every three or four tests to establish the change in rate of carbon formation as the engine wears and as the piston-ring seal changes. It may be desirable every eight or ten runs to remove pistons for cleaning ring grooves and instal new rings. Reference oil runs should precede and follow any such step.
5. Carbon accumulations should be collected for each cylinder separately and considered as a separate test. Deposits should be weighed as collected and again after drying or removal of excess oil. It may be desirable to keep piston-crown carbon distinct from the accumulation in the remainder of the combustion chamber as an index of the effect of surface temperature.
6. The effect of oil viscosity on carbon may be misleading unless the amount of oil pumped and the ratio of bypass to pump-delivery quantities is taken into consideration. A special set-up involving flow meters and possibly dry-sump operation may be necessary to go into this refinement.
7. Some oils form carbon at different rates although the final amount may be the same on an extended test.
8. For a complete investigation the effect of fuel, load, speed, engine temperature, materials of construction, oil-flow rate to engine, ignition timing, humidity, mixture ratio, &c., should not be overlooked.
9. The age of the oil in the crankcase may affect carbon formation. It may be desirable to run new oil and used oil in clean engines to determine the results for the customer who changes oil frequently compared to the user who runs long periods between drainings.
10. Chemical analysis of carbon deposits are essential for a strictly research type of investigation. Certain fuels form heavier deposits than others and a large portion of such deposits are not carbon or hydrocarbons.

11. It will be essential in most cases to determine oil consumption accurately on all carbon accumulation tests. The length of test must be a compromise between that necessary to obtain measurable and accurate oil consumption and that for obtaining near equilibrium carbon accumulation. The equivalent of 2,000 miles driving is recommended.

V. Wear

Engineers are divided in their opinion regarding both the seriousness of engine wear, particularly cylinder and cylinder-liner wear, and the causes thereof. Service results are inconsistent and in cases of excessive wear it is usually difficult to ascertain the exact reason. As an example, a 1934 eight-cylinder car in the lower-price class recently completed a road test in normal every-day service with an average cylinder wear of 0·0008 in. in 32,000 miles. In contrast to this, another eight-cylinder car, 1931 model, running on the same brands of fuel and lubricant, covered approximately 20,000 miles in 4 years and required a major overhaul due to excessive wear. The difference may probably be attributed to improvement in cylinder metals and cylinder-finishing methods in the more recent models; the longer period of time, and probable lower operating temperature causing more corrosive action in the latter case; plus variations in miles run per crankcase draining, engine-operating temperature, average-load factor, and the like. Taxicabs and house-to-house delivery cars usually show higher wear than cars operating at high-load factors. Tractor engines in dusty agricultural service have been known to wear out in less than two-weeks' operation when not equipped with adequate air filters, yet railcar engines frequently run over 100,000 miles without excessive wear. Sulphur has been blamed for excessive wear, yet for years many West Coast gasolines of unusually high sulphur-content have been used in all kinds of climates and temperatures without observing any unusual wear. Obviously, a great deal is still to be learned regarding the factors affecting wear in actual service.

We are just now reaching a point where it seems probable that wear in the generally accepted interpretation of the term is more a matter of chemical activity and corrosion than it is of mechanical abrasion and the role of the lubricant as such may be of secondary rather than primary importance. Just how far the physical and chemical properties of lubricants can counteract the corrosive wear action must yet be determined. The contributions of Ricardo and of the Institute of Automobile Engineers on cylinder wear are outstanding among the more recent published work on this important problem. For the reader interested in conducting experiments on wear, the technique and general method of attack employed by the I.A.E. Committee should be of invaluable assistance. (See Bibliography.)

For slow-speed engines the method of collecting the oil from the cylinder walls for extraction of metals offers an excellent means of determining wear and studying the various factors entering into its quantitative significance. This method has been adapted to high-speed automobile engines by Professor Everett of the experimental station at Pennsylvania State University, State College, Penn., with considerable success. Although the exact method and results have not yet been published, the preliminary data obtained indicate that the method should be valuable in this type of research.

For the casual investigator and the equipment operator who desires to know the amount of wear occurring, the relatively simple measurement of piston-ring wear may suffice as an index of general cylinder-wall wear. Cylinder wear itself is not always easy of determination. Except in special cases such as in certain marine service where low-engine temperatures accelerate wear, or in industrial and farm-tractor equipment where dust may cause rapid wear, the time required to produce a measurable amount of wear is too great to be of value in a research investigation.

When using piston-ring wear as an index of cylinder-wall wear, two methods may be used. The first involves weighing the rings on a chemical balance before and after a test, the loss of weight being a measure of the resulting wear. The second method is usually more adaptable to the average case. It requires machining a ¼-in. bore in a block of steel to the exact size of the original cylinder bore. By slipping each ring into this block and measuring the end clearance with feeler gauges, the increase in ring-gap clearance is determined for each test. Care must be used to ensure that the parts are always at the same temperature when measurements are made. It should be pointed out that piston-ring wear is not definitely indicative of wear on other parts of an engine.

While there exist many excellent tools for measuring the size of parts—particularly the bore of cylinders—in all likelihood a skilled mechanic with an ordinary set of micrometers and thickness gauges is still the most satisfactory means of obtaining accurate measurements.

In conclusion, the authors wish to emphasize that the foregoing material has been submitted more in the nature of suggestions than as fixed and rigid rules to be followed. Space has limited us to only the essential details. It is hoped that the suggestions made will stimulate interest and thought on the various topics covered and that the ultimate result will be a worthwhile improvement in the work of the varied industries and individuals engaged in this endeavour.

SELECTED BIBLIOGRAPHY

BAHLKE, W. H., BARNARD, D. P., EISINGER, J. O., and FITZ SIMONS, O. Factors Controlling Engine Carbon Formation. *J.S.A.E.* **29**, no. 3, 215 (1931).

BLACKWOOD, A. J. Engine Performance at Low-operating temperatures. *J.S.A.E.* **36**, no. 2, 70 (1935).

BLACKWOOD, A. J., RICKLES, N. H. Cold-starting Characteristics of Automobiles. *J.S.A.E.* **28**, no. 2, 234 (1931).

CRUSE, W. A. Carbon-forming Tendencies of Lubricating Oils. *World Petr. Cong., London, Proc.* **2**, 441 (1933).

JEHLE, FERDINAND. Laboratory Technique, Methods and Equipment. *J.S.A.E.* **19**, no. 4, 373 (1926).

MARLEY, S. P., LIVINGSTONE, C. J., CRUSE, W. A. Influence of Temperature, Fuel and Oil on Carbon Deposition. *J.S.A.E.* **18**, no. 6, 607 (1926).

MOUGEY, H. C. Oil Consumption as Affected by Engine Characteristics. *J.S.A.E.* **29**, no. 3,200 (1931).

O'NEILL, J. G. Work Factor of Lubricants. *Trans. Amer. Soc. Mech. Engrs.* **53**, no. 16, 41 (1931).

RICARDO, H. R. Some Notes and Observations on Petrol and Diesel Engines. *J. Inst. Auto. Engrs.* March 1933, p. 13; June 1933, p. 45.

UPHAM, E. W., GRAVES, W. H., MOUGEY, H. C. Winter Oils for Automobile Engines. *J.S.A.E.* **35**, no. 2, 238 (1934).

WILKIN, R. E., BARNARD, D. P., BARNARD, E. R., ROGERS, T. H., SHOEMAKER, B. H. Causes and Effects of Sludge Formation in Motor Oils. *J.S.A.E.* **34**, no. 5, 167 (1934).

WILLIAMS, C. G. Interim Report of the Research and Standardization Committee on Cylinder Wear. *J. Inst. Auto. Engrs.* June 1933, p. 73.

—— Further Experiments on Cylinder Wear. *J. Inst. Auto. Engrs.* **2**, no. 10, 19 (Aug.-Sept. 1934).

Also the following two papers, as yet unpublished but presented at the International Automobile Engineering Congress of the Society of Automotive Engineers, Chicago, Illinois, 28 August to 4 September 1933, are noteworthy. They are abstracted and discussed in the *J.S.A.E.* **33**, no. 4, 42.

(*a*) LICHTY, L. C.; CARSON, G. B. Engine Friction Analysis.

(*b*) STEWART, J. P.; RISK, T. H. Factors Affecting Oil Consumption.

ENGINE TESTS OF LUBRICANTS

By C. H. BARTON, M.A., A.I.C., M.Inst.P.T., and O. THORNYCROFT, O.B.E., B.A., M.I.Mech.E.
Asiatic Petroleum Company, Ltd. *Ricardo & Co., Ltd.*

Introduction

Of all the properties of a lubricating oil that may be determined in a chemical laboratory, the only one directly related to the performance of the oil in an internal-combustion engine is the viscosity-temperature curve. Starting-torque, engine friction, and rate of oil circulation and consumption are all affected to a greater or less extent by the viscosity of the lubricant at the relevant temperatures. On the other hand, the remainder of the tests which are commonly applied to the examination of unused motor oils afford either indirect or negative information in regard to the performance of lubricants.

In addition to viscosity measurements, the tests applied to unused lubricating oils may be classified as follows:

(*a*) Tests for contaminants and undesirable substances such as water, dirt, and acidity.
(*b*) Examination for the presence of fatty oils and dopes.
(*c*) Identification tests which may give some indication of the origin of an oil. Such tests include specific gravity, flash-point, and other physical and chemical determinations.
(*d*) Tests which are intended to provide information on the performance of oils.

Some of the tests in the latter category, such as those for volatility, oxidation-stability, and carbon residue, may, when cautiously interpreted, afford a useful insight into the relative performance of oils. On the other hand, attempts to deduce too much from them may lead to erroneous conclusions. For example, the frequent assumption that low stability towards oxidation (as determined by an arbitrary oxidation test) necessarily implies a high rate of sludge formation in a crankcase oil is not supported by engine results. The explanation of the lack of concordance between laboratory results and engine tests is that the former are obtained by methods which, up to the present, have not succeeded in reproducing the complex conditions of oxidation, cracking, and evaporation to which a lubricating oil is submitted in the engine. Thus, oxidation tests [52, 1934; 66, 1928] which are commonly carried out at temperatures in the neighbourhood of 200° C. cannot be expected to produce the same effects in an oil as the treatment which it undergoes in use, a treatment which includes low-temperature oxidation in the crankcase at one extreme and exposure to flame temperatures in the combustion space at the other. When it is recalled that high oxidation stability in an oil is frequently accompanied by relatively low resistance to cracking conditions at high temperatures, it is not surprising that a simple oxidation treatment produces effects very dissimilar to those observed in the engine.

To the difficulty of reproducing in the laboratory the conditions under which oils are decomposed in the engine is added the problem of evaluating the changes brought about by heat and oxidation. These considerations lead to the question of testing used oils, a subject which must be dealt with before that of oxidation tests is further discussed.

The examination of used oils in the laboratory is a matter in which relatively little standardization has been achieved, as is shown by the fact that the standard methods of the I.P.T. and A.S.T.M. contain only one test specifically drawn up for used lubricating oils, viz. that for determining fuel dilution in crankcase oils from gasoline engines. The tests generally applied to used oils, in addition to the dilution test, include viscosity measurements, specific gravity, ash determination and analysis, examination for acidity, and the application of various precipitation tests, carried out by adding definite proportions of such liquids as petroleum ether, benzene, or chloroform. The precipitated solid substances obtained from used oils in these tests are referred to variously as 'sediment' (petroleum ether or benzol insoluble), 'asphaltenes' (soluble in benzol or chloroform, insoluble in petroleum ether), 'carbon' (benzol or chloroform insoluble), 'varnish' (insoluble in petroleum ether, soluble in ethyl alcohol), &c. Unused oils give negligible precipitates with these solvents.

The 'varnish' or 'lacquer' [11, 1930; 13, 1933] content of a used oil is provisionally defined as that part of the petroleum ether insoluble material which is soluble in ethyl alcohol. Varnish is distinguished from wax by the fact that it is soluble in cold alcohol. 'Varnish' is so sparingly soluble in lubricating oil that only minute amounts are found even in oils from compression engines in which this type of material is most commonly formed owing to defective combustion conditions. The substances obtained in the remaining precipitation tests are produced by the oxidation and heat treatment of the oil during use, with the probable inclusion of carbon particles formed on the underside of the pistons and a certain amount of ash. The latter may be eliminated, as far as large particles are concerned, by filtering the used oil through wire gauze before adding the precipitant. Alternatively, the total 'sediment' obtained by addition of, say, petroleum ether, may be extracted with a solvent, such as benzol, which dissolves the 'asphaltenes' and leaves behind the 'carbon', i.e. the material of highest carbon content.

Although the actual amounts of material obtained from a used oil vary considerably according to the precipitating solvent used, there is generally a rough proportionality between the 'sediments' produced by the various solvents from a series of used oils when allowance is made for the mineral matter (ash) present. Thus petroleum ether almost invariably gives a greater amount of insoluble material from a mineral or compounded oil than is found when benzol is employed as the precipitating solvent. It is perhaps unnecessary to point out that care must be taken in sampling a used oil if the 'sediment' measured is to be representative of the bulk of the oil.

The various 'sediment' tests, as they may be conveniently called, are virtually alternative methods of obtaining some measure of the relative amounts of solid substances, formed by changes in the oils during use, and insoluble in the particular solvent used. With the limitation that they take no account of soluble substances, the results of sediment tests serve as a useful basis for comparing the extent to which oils have changed chemically in service. It will, however, be shown in the section dealing with sludge that the percentage of sediment in a used oil is not necessarily a measure of the tendency of an oil to form sludge deposits, to block filters, and to produce a dirty engine. The failure of sediment results to indicate oil performance satisfactorily is, in part, due to the fact that oils having a pronounced tendency to form sediment generally possess a correspondingly increased solvent action on the sediment. Moreover, the examination of actual sludge deposits shows that the sediment present is only a proportion of the total mass, sometimes as little as 10 or 20% of the whole. It is sometimes observed that an oil of high stability which produces a relatively small amount of sediment in use gives partially blocked oil filters more rapidly than a less stable oil, owing to the low solubility of the sediment in the oil. Generally speaking, the least trouble from sludge deposition is given by oils which have the most pronounced tendency to remain homogeneous in use. It follows, therefore, that to attempt to estimate the sludge in a used oil by adding precipitating materials which change the solvent properties of the oil is wrong in principle.

To return to the question of oxidation tests on unused oils, it follows, from what has been said concerning the difficulty of testing used oils, that the assessment of the results of oxidation tests, which almost inevitably fail to reproduce the treatment of oils in the engine, is not an easy matter. It is possible to devise oxidation tests that will grade oils according to the rate at which they form asphaltenes in use in a test engine. Since the connexion between relative asphaltene production and the performance of oils is not known, not much practical information is obtained from oxidation tests.

The most important piece of work on the correlation of rate of asphaltene formation in oxidation tests and in a standard bench engine is that of Barnard [6, 1934] and his colleagues, who found that the rate of asphaltene formation in a series of oils oxidized under controlled conditions at 341° F. was relatively similar to that which took place in the engine. These results are of great interest, but it is hardly safe to assume without proof, as these authors have done, that the asphaltene contents of used or oxidized oils are a direct measure of the sludging properties of the oils.

It will be necessary to revert to the testing of used oils when discussing sludge formation and the changes that occur in oils during use.

Engine Test Methods

It is of the first importance, in making engine tests of lubricants, that means are provided to maintain a constant rate of oil consumption and the rate must be accurately measurable. Because of the need for the control and measurement of oil consumption, a single-cylinder engine is much to be preferred to a multi-cylinder one.

The speed of engine rotation is relatively of little importance, since temperature and time are the supreme factors which determine the chemical changes that take place, and both temperature and time may generally be controlled independently of engine speed. It may be accepted that the pressures and velocities to which the lubricant is exposed in an engine do not, in themselves, effect any change in the oil. Engine speed, on the other hand, has a very considerable effect on oil consumption, and if, for the reason of preserving the life of the engine, it is desirable to employ a relatively low rotational speed, it may be necessary to increase artificially the rate of oil consumption. This may be conveniently accomplished by a jet of oil directed upon the connecting-rod or into the mouth of the cylinder. The rate of flow at the jet should be controllable and measurable so that constant conditions of feed may be maintained. A valuable method of measuring oil consumption continuously in a bench engine has been described by Stewart and Risk [57, 1933].

It may sometimes be useful to examine oil that has been exposed to the conditions on the cylinder wall but which has not become mixed with the more complicated contents of the crankcase. For such an experiment a 'crosshead' type of engine is used. The crosshead may be lubricated by oil-throw from the big-end bearings, but care should be taken to prevent any but small quantities of oil reaching the space above the crosshead. An independent and measured quantity of oil is fed to the cylinder through holes drilled near the level of the piston rings at bottom dead centre. Most of the oil spread in this way upon the wall of the cylinder reappears in the crosshead chamber and thence is led by piping to a collecting vessel.

It is seen, in this arrangement, that the rate of oil consumption may be accurately controlled and measured, and, furthermore, the rate at which oil is received by the cylinder wall may be exactly observed.

The duration of each test has generally to be determined by preliminary experiment. The time should be as short as possible so that the mechanical depreciation, and consequently the uncontrollable change of conditions from one test to the next, shall be as small as possible. The length of each test should, however, be sufficient for equilibrium to be nearly established in the carbon deposits. This requirement involves on many engines a test of at least 20 hours.

In a series of tests with different oils, it will usually be found necessary to make frequent check tests on the first oil to be tested, so that the two errors due, respectively, to uncontrolled variations and the progressive change in conditions due to engine wear may be evaluated.

Much time and engine wear can be saved by providing a heater, independently supplied with energy, in the oil reservoir. By this means the temperature of the oil may be raised nearly to the stable running temperature before each test is commenced.

In order to shorten the period of each bench test it may, in certain cases, be justifiable to increase the severity of the temperature conditions well beyond those that would occur in service. In the study of the phenomenon of ring-sticking, experiments have been made on the test-bed by using an air-cooled motor-cycle engine, the temperature being controlled by varying the velocity of the cooling air. In these tests the temperature conditions may be made very severe by running the engine at full throttle and at a high speed, and by reducing the wind speed until such a cylinder temperature is reached that ring-sticking is produced in less than 10 hours of running. Furthermore, by modifying the knock-rating of the fuel the effect of detonation may be explored.

It may be said with some justice that oil tests in the laboratory cannot reproduce the conditions of actual use in, for example, vehicles upon the road. The load and speed, and therefore the temperatures and rate of oil consumption, are constantly varying in an engine used for transport purposes, and it is practically impossible to reproduce such variable conditions on the test-bed. On the other hand, it is quite impossible to make accurately repeatable tests on the road and, since only small differences in behaviour are generally to be looked for, the need of repeatability must be put before anything else.

Road tests, nevertheless, must be employed in order to gain knowledge of the conditions to be reproduced, so far as possible, on the test-bed. Crankcase and cylinder temperatures, also oil consumption and oil contamination (with condensed water and fuel), should be measured for typical vehicles and various service conditions. Either the average or the maximum road temperatures can easily be provided in the bench tests; the oil consumption also may be adjusted to represent the average road conditions, and both water and fuel, in proportions that have been observed in road tests, may be added to the lubricant at regular intervals in the course of each laboratory test.

In the following sections some details will be given of the various aspects under which lubricating-oil performance has been studied by means of engine tests. It will be seen that, with regard to some of the subjects, such as carbonization and performance at low temperatures, many of the factors and their effects are well known; but on other questions, such as the changes which take place in oils in use, a great deal remains to be cleared up.

Carbonization

The name 'carbon' is usually applied to the black deposits which form by decomposition of lubricating oil or by incomplete burning of the fuel in the combustion space of an internal-combustion engine. The deposits may vary in consistency from hard and brittle to soft and friable or oily material. Hard deposits on the underside of the piston, on the valves, and in the piston-ring grooves are usually also referred to as carbon.

Carbon deposits contain varying amounts of ash, derived from the dust of the ingoing air and wear of the metal surfaces of the engine, together with considerable proportions of oil which may be extracted by petroleum ether [42, 1926; 58, 1930]. The remainder of the deposit contains a proportion of the element carbon, but is far from being pure carbon in the chemical sense. Most investigators use the term 'carbon' to mean the complete deposit as it is formed in the engine, and it is in this sense that the term 'carbon' will be applied in this article, since it is the deposit as a whole which is important in regard to its effect on the behaviour of the engine [3, 1931]. Subtraction of the ash content, obtained by ignition of the deposit, will not, in most cases, make much difference to the weights of carbon reported, since the ash is generally not more than 5% of the total deposit; but correction for the oily constituents by extraction with, say, petroleum ether may make an appreciable difference to the reported weights of the carbon deposits, since the oil content is affected by the rate of oil consumption and may vary from 10 to 30% or more of the total deposit.

In regard to carbonization, engines fall into two classes: those in which carbon formation is important, and those in which carbon formation is relatively unimportant and does not, by itself, seriously affect the performance of the engine and make overhaul necessary before valves, pistons, and other working parts call for attention. Fortunately, most engines belong to the second category and may be lubricated with oils of relatively high carbonizing tendency without serious impairment of their performance by carbon deposits. In the most sensitive engines of the first category it is essential to avoid the use of oils of high carbon-forming characteristics, since the resulting deposits on the pistons and valves necessitate frequent cleaning of the engine to maintain its performance.

The numerous factors which control the formation of carbon deposits have been listed by Gruse [24, 1933]. They include engine design and condition, the running conditions, the rate of oil consumption, the properties of the lubricant, the air-fuel ratio, the time since cleaning, the amount of dust in the air, and the characteristics of the fuel. Of these factors, the first four are generally more important than the last four. The 'time since cleaning' is not of great significance except in engines in which running is seriously affected by the presence of carbon. There is considerable evidence [3, 1931; 24, 1933; 14, 1926; 58, 1930] that carbon deposits tend to reach an 'equilibrium' after 20–50 hours' running, provided that running conditions remain stable, the amount of the deposit depending upon the factors enumerated above. An engine sensitive to carbonization will require cleaning before the full equilibrium amount of deposit has been produced, i.e. generally before it has completed 20 hours' running. That the majority of engines will perform satisfactorily for much longer periods is a matter of observation which is explicable on the notion of a state of equilibrium in carbon deposition.

Insufficient information is available to form a basis for generalizations on the effect of engine design on carbon formation, but it is known that increasing turbulence of the charge sometimes promotes carbon deposition. Engine condition is chiefly important in regard to its effect on rate of oil consumption, which will be discussed below. Of the working conditions, the principal ones affecting carbonization are load, temperature, and, less important, detonation. In any particular engine the first two normally vary together in the same sense. Detonation may, of course, be regarded as partly a fuel effect. Generally speaking, carbon deposits increase with load and combustion surface temperatures up to a maximum, and then fall with further increase of load [3, 1931]. Detonation appears to reduce the amount of carbon formed on the top of the piston, but has a tendency to increase the amount of deposit in the top piston-ring groove, a part of the engine in which carbon deposits are more dangerous than they are on the piston crown. The following results, obtained in a small air-cooled single-cylinder engine running at 3,000 r.p.m. and full throttle (100 lb. per sq. in. B.M.E.P.), are typical of a large number of similar results.

TABLE I

Duration of test, hr.	10	10
Cooling wind speed, m.p.h.	62	46
Cylinder barrel, temp.° C.:		
At top	230°	230°
At middle	171°	175°
At bottom	152°	152°
Fuel: knock-rating	47 octane number (giving detonation)	74 octane number (no detonation)
Fuel consumption, pints per hr.	4	4
Carbon on piston, g.:		
Crown and top land	0·17	0·40
Top ring groove	0·43	0·25
Bottom ring groove	0·09	0·02

Approximately the same total amount of carbon was obtained in each test, but in the first test, with detonation, the greater part of the carbon deposited in the ring grooves. The top ring was stuck in this test, whereas it was quite free in the non-detonating test. The same lubricant was used throughout and the engine was cleaned between each run.

In most engines the rate of oil consumption has an important influence on carbonization, and it is generally found that, up to a fairly high rate of consumption, the amount of carbon deposited is proportional to the quantity of oil consumed [24, 1933; 61, 1931]. A further increase in the rate of oil consumption then produces no greater amount of carbon and may even reduce the quantity of deposit. This is illustrated by the following results of 20-hour tests in a single-cylinder water-cooled bench engine running on the same lubricant under similar conditions throughout, except that the rate of oil consumption was varied by adjustments to the relief-valve of the pump.

TABLE II

Oil consumption, pints in 20 hr.	0·92	1·41	2·27	2·60
Carbon on piston, crown, g.	0·32	0·54	0·34	0·47
Carbon on piston, crown, g. per pint of oil consumed	0·35	0·38	0·15	0·18

The nature of the lubricating oil has a considerable influence on the amount of carbon formed in the combustion space. Generally speaking, distillates produce smaller deposits than residual oils and blends thereof [3, 1931; 58, 1930; 43, 1927]. Numerous chemical and physical tests have been proposed for evaluating the carbon-forming tendency of lubricants. Those most frequently applied are coking tests of the type of the Conradson and Ramsbottom tests. Some workers find that good correlation is obtained between coke tests and engine carbon deposits [24, 1933; 25, 1931; 42, 1926], but the correlation invariably breaks down when a wide variety of oils is examined [3, 1931; 32, 1933]. The presence of fatty oils also tends to upset the relationship between coking tests and engine carbons, since the addition of fatty to mineral oil usually reduces the coke result and increases the amount of carbon in the engine. The failure of coking tests has led some investigators to propose a vacuum distillation test [3, 1931; 24, 1933; 38, 1929] in which the temperature required to distil a high proportion, say 90%, of the oil under a pressure of 1–10 mm. mercury is determined. The higher the temperature reached in the distillation the greater is the carbonizing tendency of the oil. There is no doubt that such a test, which is based on the conception that carbon deposits in the engine are largely formed by decomposition of the least volatile fractions of the lubricant, correlates better in some cases with engine results than do coke tests. A coking test in the presence of air has also been described [51, 1933], in which oil is dropped at a controlled rate into a metal chamber through which a measured stream of air passes, the whole being maintained at a definite temperature between 350° and 500° C.

A coke test which reproduces the relative carbonizing tendency of all lubricants is probably an unattainable ideal, if only for the reason that different types of oil react differently to varying engine conditions with regard to carbon formation. The types of coke or carbon tests which have been mentioned, however, are capable of yielding useful information for the selection of lubricants of low carbonizing tendency, particularly when a choice has to be made between the possible blends of two or three basic oils. In such cases, coking tests are commonly in line with engine carbonization.

Although it is not known how much of the total carbon deposit in the combustion space is due to incompletely burnt fuel, evidence has been obtained that carbon formation increases with the fuel-air ratio in a gasoline engine [42, 1926; 58, 1930]. Little systematic work appears to have been done on the subject with compression-ignition engines, but it seems probable that carbonization decreases as the load increases. Reference is made in a later section of this article to the formation of sludge-like substances under conditions of poor combustion in C.I. engines.

No data has been published on the effect of dirt in the air on carbon deposits, but it is probable that in engines working under very dirty conditions, as in the case of tractors on light, dry soil, the amount of carbon deposited is considerably increased by the presence of dirt.

The volatility of gasoline has a negligible effect on carbonization [24, 1933], but low volatility fuels, such as kerosine, and white spirit, appear to produce more carbon than is found with gasolines. Interesting results on the behaviour of gum-bearing cracked gasolines have been obtained by Marley and Gruse [24, 1933; 41, 1932]. It was found that when the intake temperature was high (about 175° F.), a gasoline of high existent or preformed gum content deposited its gum in the induction pipe and gave no increase in combustion-chamber carbon. With a cold or unheated intake there was practically no deposit in the manifold, but a small increase took place in the carbon in the cylinder.

The hardness of carbon deposits depends very much on engine temperatures and rates of oil consumption. Fatty oils and their blends with mineral lubricants commonly give harder deposits than do pure mineral oils. Amongst the latter, distillate oils generally produce softer deposits than are formed with residual oils. In some engines it is found that the hardness of a deposit increases with the quantity formed [3, 1931].

Alteration of Lubricating Oils during Use

The tests commonly applied in the laboratory to used lubricating oils may be roughly classified into two groups: namely, those for detecting contamination, such as fuel diluent, ash, and water; and those intended to determine the physical and chemical changes in the oil itself, after removal, if necessary, of the contaminants. Sludge in a used oil may be regarded both as contaminating material, and, in so far as it remains in suspension or solution, and increases the viscosity of the oil, it may also be considered as part of the oil. When it is desired to carry out tests on the oil and sludge together, the tendency of the sludge to settle out from oil on standing must be kept in mind. Sludge is discussed in some detail in another section of this article, and attention may therefore be directed to the remaining constituents and properties of used oils.

Of the contaminants in used oils, only the mineral ash can possibly depend in amount on the nature of the lubricant, since the latter may have an effect on the rate of engine wear. The metallic oxide constituents of ash do not appear to have abrasive properties, but when more than about 10% of silica is found in the ash of a used oil, the possible presence of abrasive material, such as sand, should be investigated. Further reference to the ash content of used oils is made in the section dealing with wear.

The proportion of diluent in a used oil depends upon the mechanical state of the engine, the running conditions, the degree of richness of the fuel-air mixture, the volatility of the fuel, but not to any appreciable extent on the nature of the lubricant. An important difference between gasoline and compression-ignition engines is that the proportion of diluent in the former reaches an equilibrium in the crankcase oil after a few hours' running [67, 1926; 20, 1924], but tends to increase continuously with time in those types of compression ignition engines that give more than 2 or 3% fuel dilution of the crankcase oil.

The chief evil of high dilution is probably the reduction [17, 1933] which is caused in oil viscosity and the consequent increase in oil consumption. It has been thought that rate of engine wear increases rapidly with high dilution of the lubricant, but Mougey [47, 1928] found that the addition of 50% kerosine to a lubricating oil did not increase wear in bench tests, and Williams [64, 1933] found that, even with abrasive dust added to the lubricant, the presence of kerosine in the lubricating oil had no appreciable effect in the rate of wear of the cylinder and piston rings until more than 60% kerosine was included in the lubricant.

The occurrence of water in crankcase oil is due to condensation from gases passing the pistons, or to leakage from the water jacket. The effect of water on sludge deposition is mentioned elsewhere. Although the presence of a small percentage of water in crankcase oil [15, 1924] does not appear to have any detrimental effect on lubrication, it may promote corrosion [47, 1928], especially if sulphur acids, derived from exhaust gases, get into the crankcase. The presence of mineral acids is indicated when the *pH* value of a used oil falls below 3.

The changes which take place in an oil in use, due to oxidation and decomposition, may be followed by viscosity measurements [61, 1931; 6, 1934], 'sediment' tests [6, 1934; 43, 1927], by diluting the used oil with solvents, tests for organic acidity [17, 1933; 45, 1927], and increase in coking value [17, 1933]. In Germany 'tar value' (Teerzahl) [30, 1924] and its related tests have been applied [19, 1930; 37, 1932]. Some of these determinations give valuable comparative indications of the changes which have taken place in oils in the engine. The limitations of sediment tests when used for estimating sludge are described in the section dealing with sludge.

It is not possible, generally speaking, to give limits, in terms of the above tests, for the maximum permissible extent to which an oil may be allowed to change in service before it is considered unfit for further use. The various test methods do not always agree with regard to the amount of deterioration which they indicate in used oils. Under normal service conditions, the fact that fresh oil is added from time to time to make up for consumption losses tends to counteract the changes in crankcase oils.

Most lubricating oils increase in viscosity in use, but it is necessary to remove, by distillation, any fuel diluent present, or to determine the proportion of diluent and correct for its effect on viscosity before the change in this property can be measured. Although oils seldom increase in viscosity at 60° C. by more than 50% in gasoline engines, in compression-ignition engines very considerable increases in viscosity are sometimes produced by the accumulation in the oil of materials from partially burnt fuel. These oxidation products, which assist in sludge formation, have been found, in extreme cases, to cause the viscosity of the lubricant, measured at 60° C., to rise to 5 or even 10 times its initial value when the oil has been in service for a few thousand miles on the road. The fact that removal of the fuel products by filtration or precipitation often leaves the oil nearer to the unused oil in physical properties than a similar treatment applied to an oil from a gasoline engine, indicates that the deterioration in such cases is essentially contamination.

The accuracy of measurement of the viscosity of used oils is generally less than that possible in the case of unused oils owing to the fact that the former are often not homogeneous.

The determination of the organic acidity of a used oil does not, as a rule, give much useful information. The acidity, expressed in terms of the equivalent amount of oleic acid, does not usually exceed about 3%, except in oils containing fatty matter. There is no evidence that the organic acids normally produced from mineral oils during service have corrosive properties, but those formed by fatty oils may attack metals, particularly copper and its alloys, when present to the extent of about 4% or more in the lubricating oil.

Sludge Deposits, Engine Cleanliness, and Piston-ring Sticking

The term 'sludge' is applied to the pasty, semi-solid deposits which are sometimes found in the crankcase, on the oil filters, or in the hollow crankpins of an internal-combustion engine. Sludge should not be confused with pieces of carbon that may be formed on the underside of the piston and drop off into the crankcase where they deposit as brittle flakes. Solid substances precipitated from used oils by addition of solvents are sometimes described as sludge; but, as pointed out earlier in this article, these precipitates or 'sediments' are not necessarily proportional to the amount of sludge in an oil.

There are several possible ways of separating and measuring sludge in used oils. The first method which suggests itself is that of leaving an oil in circulation in an engine until sludge deposits form. This method is not generally suitable for oil-testing purposes owing to the long running periods required for the formation of deposits and the difficulty of collecting and measuring the sludge. Observations may, however, sometimes be made with vehicles running under controlled service conditions, particularly when sludge deposits in definite parts of the engine from which it may be collected, such as hollow crankpins and sump filter pads. A second method, which has been used by the authors [58, 1930; 43, 1927], employs a centrifuge through which the oil is continuously circulated while the engine is running. Although useful results may be obtained on bench tests with this method, it is necessary to run for at least 50, and with some oils for 100 or more, hours to obtain reasonable quantities of sludge for weighing. Even with a centrifugal force of about 1,500 times that of gravity the rate of removal of the sludge from the oil at 50° C. is slow, so that if the centrifuge is stopped when the engine is shut down, a proportion only of the total quantity of separable materials has been removed.

A method of sludge estimation which the authors have found convenient consists in filtering with suction a used oil through a fairly coarse filter paper in a Buchner funnel maintained at about 80° C. by means of a water jacket. A convenient form of apparatus made principally of metal is shown diagrammatically. The filtration method gives results with oils which have undergone relatively little deterioration in use, but is difficult to apply in some cases when appreciable amounts of water are present. The oily deposit on the paper may be weighed as such or first washed with a solvent to remove the more oily portion. If required, the ash content of the deposit may be determined by ignition. It is important to point out that washing the sludge deposit with a solvent such as petroleum ether is not equivalent to treating the whole of the used oil with the same solvent. This is shown by the results given in the fourth and seventh lines of Table III, which summarizes the results of 20-hour tests on three different mineral oils, *A*, *B*, and *C*, in a water-cooled, single-cylinder bench engine. No fresh oil for 'make-up' was added in these tests.

TABLE III

Test No.	*1*	*2*	*3*	*4*	*5*	*6*
Oil	*A*	*A*	*B*	*B*	*C*	*C*
Oil consumption, litres	0·51	1·31	0·51	1·6	0·85	1·71
'Sediment', % by wt. insoluble in 60°/80° petroleum ether	0·27	0·55	0·16	0·32	0·14	0·17
'Asphaltenes', % by wt. (portion of 'sediment' soluble in benzene)	0·21	0·39	0·02	0·05	0·04	0·03
Oily sludge, by filtration, g. per litre	3·5	7·4	1·9	2·8	3·2	4·0
'Sediment' in sludge (insoluble in 60°/80° petroleum ether), calculated as percentage by wt. of used oil	..	0·22	0·05	0·12	0·10	0·12
Ratio: $\frac{\text{sludge (from line 6)}}{\text{sediment (from line 4)}}$	13	13·5	11·9	8·8	23	23·5

The oil consumptions in the above tests were controlled by changing the pressure on the relief valve of the oil pump. The results show that there is no simple relation between the sediment or asphaltene contents of the used oils, on the one hand, and the amounts of sludge removable by filtration, on the other hand. For each oil, however, the sediment and asphaltene figures are roughly proportional to the sludge contents, and may therefore be used to indicate the relative amount of sludge present in different used samples of the same oil.

Of the three oils mentioned in Table III, oil *A* is the least resistant to oxidation treatment, oil *C* is the most resistant, while oil *B* is intermediate between *A* and *C* in this respect. Comparison of the sediment or asphaltene results (lines 4 and 5) with the respective sludge figures (line 6) of each used oil shows that, for a given proportion of either of the former, oil *B* contains less sludge than oil *A*, and oil *A* contains less sludge than oil *C*. This point is illustrated by the figures of the last line of the table. In the case of these oils, therefore, the one of highest stability has relatively the lowest solvent effect on its sludge products.

It has been suggested [58, 1930; 34, 1933; 17, 1933; 38*a*, 1936] that the origin of sludge-forming substances lies mainly in the decomposition products formed in the combustion space from the oil and, particularly in compression-ignition engines, from the fuel. The break-down of oil in the engine is hastened by intimate mixing with the hot gases in the cylinder, due to spraying of the oil which passes the piston. Some of the oil drops are more or less completely burnt and pass out with the exhaust gases, but others deposit their products on the cylinder walls and piston crown, and thence find their way back to the crankcase. This picture of the origin of crankcase sludge is supported by the following observations:

(1) General decomposition of the lubricant and sludge formation, excluding the effect of water in the crankcase, is as rapid in a water-cooled as in an air-cooled engine of similar capacity and rate of oil consumption.

(2) The rate of formation of decomposition products in a crankcase oil increases with oil consumption [21, 1926; 61, 1931], owing to the greater rate of circulation of oil between the crankcase and combustion space. This is illustrated by the results of Tables III and IV. The latter table deals with tests on oil *A* in the same water-cooled engine referred to in Table III. No fresh oil was added during a test.

TABLE IV

Test No.	*1*	*7*	*8*
Oil consumption, litres	0·51	0·74	1·48
Oily sludge in used oil by filtration, g. per litre	3·5	9·6	29
Total sludge in crankcase oil, g. at end of 20 hr.	14	15	23
'Sediment', % by wt. in used oil	0·27	0·40	2·2
Engine speed, r.p.m.	900	900	1,100

In test no. 1 the quantity of oil put into the engine was double that of tests 7 and 8, and the amount of oil remaining at the end of the run was therefore the greatest in test no. 1. It is evident that not only the concentration but also the total amount of sludge tends to increase with the oil consumption. Under ordinary service conditions in which fresh oil is added to the crankcase at intervals to compensate for oil consumption the effect of a high rate of consumption on oil deterioration is, naturally, masked to some extent. When the consumption of oil is very high, the regular addition of the full amount of fresh 'make-up' oil does not suffice to keep the oil as clean as it would be after a normal period in use under conditions of low consumption.

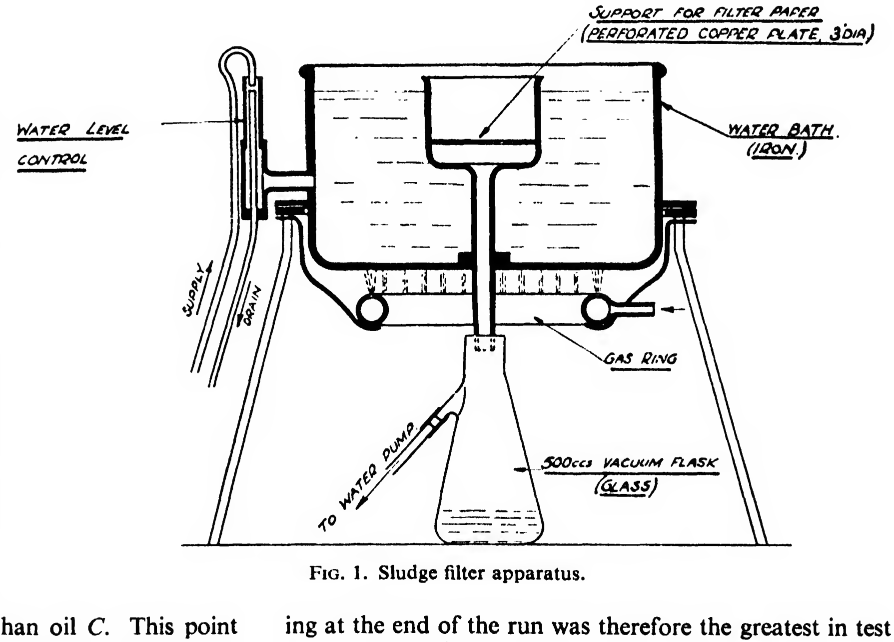


FIG. 1. Sludge filter apparatus.

(3) In an engine fitted with a crosshead piston, and direct

supply of oil to the cylinder and piston, the rate of deterioration of the crankcase oil is extremely low. An engine of this type, in which the contamination of the crankcase contents by oil drainings from the piston amounts to only about 1% for each 10 hours' running, the crankcase oil shows only slight darkening in colour after 50 hours. The stability of the oil is, of course, partly due to the low oil temperatures due to the absence of contact between the piston and crankcase oil. On the other hand, the first drainings of used oil from the piston and cylinder, collected within 20 or 30 minutes of starting up, contain considerable amounts of sludge and decomposition products.

As an objection to the idea that the deterioration of oil is largely due to the occurrence of a spray of oil drops above the piston, it has been pointed out [52, 1934] that oil consumptions as low as 1 cu. mm. per cylinder per engine revolution have been recorded in large gasoline engines. Although there is no difficulty in imagining that such a minute amount of oil in the form of spray might be completely burnt, it must be borne in mind that the quantity of lubricant sprayed into the combustion chamber is, in all probability, considerably greater than the amount consumed. The case of the engine having a low oil consumption does not, without data on the rate of deterioration of the lubricant, constitute an objection to the oil-spray process. In such an engine the rate of deterioration, on the oil-spray hypothesis, should be low. If it could be shown that the rate of formation of decomposition products in the oil was as rapid at a low as at a high oil consumption, then the origin of the oil deterioration would have to be sought in either contamination with fuel products or in oxidation and cracking on the underside of the piston.

With regard to the latter point, the test results of Table V which were obtained with a single-cylinder, air-cooled engine on the bench are of interest. Each test ran for 20 hours at a cylinder-barrel temperature of 190–200° C. No fresh oil was added during either test. The lubricant was oil *A* of Table IV. In the first test an iron baffle-plate was fixed inside the piston, above the gudgeon-pin, to prevent oil from splashing on to the underside of the piston crown. Comparison of the results of the two tests shows that, in this engine at any rate, removal of the baffle (in the second test) has a negligible effect on the rate of deterioration of the oil in the engine used for these tests.

TABLE V

Test No.	*1*	*2*
Oil consumption, pints . . .	1·0	1·0 (= 0·57 litre)
Oily sludge, g. per litre in used oil .	2·8	2·8
'Sediment', % by wt. (insoluble in 60°/80° petroleum ether) . .	0·15	0·18
Baffle-plate to underside of piston .	Present	Absent

It is well known that the presence of water in used oil, due to condensation from gases blowing past the pistons, or to leakage from the water jacket, assists greatly in the separation of sludge [58, 1930; 16, 1933; 9, 1935]. The production of watery sludges is particularly noticeable in the valve [26, 1933] rocker chambers of water-cooled, overhead-valve engines, the sludge forming in thick, slimy masses on the underside of the cover. Provision of adequate ventilation is generally a complete cure for this trouble.

Apart from any water which may be present, sludge deposits generally contain a high proportion, more than 70%, of oily substances soluble in petroleum ether [26, 1933; 6, 1934; 17, 1933]. A smaller proportion of carbonaceous matter, insoluble in benzene, is also present, together with varying amounts of ash composed of metallic wear and dust. Sludge deposits become harder and less oily with time, particularly when they form in hollow crankpins and centrifuges. The chemical composition of hard sludge deposits is similar to that of carbon deposits in the combustion chamber [58, 1930].

The harm caused by sludge deposits is probably very small except when they are allowed to grow to considerable dimensions. In such cases sludge may obstruct the flow of oil at two important points, namely, at the sump filter and in the drain holes of the piston-scraper rings and grooves. Blockage of the oil filter reduces the supply of oil to the pump and causes a fall in the oil pressure, while sludge in the scraper ring holes and slots commonly leads to increased oil consumption. The sticking of the pressure rings in low-temperature engines is probably due, in most instances, to the accumulation of sludge in the ring grooves. As the rings gradually lose their freedom of movement, the blow-by of hot gases increases, and by the time that complete sticking occurs the sludge deposits have become hard 'carbon'.

The general cleanliness of piston skirts, crankcases, and valve gear is closely bound up with sludge in the sense that conditions promoting sludge formation tend to produce a dirty engine. The condition of an engine in this respect may give rise to comment, although the period of running may have been insufficient for actual sludge deposition.

In addition to the piston ring-sticking, which is sometimes brought about in low output, water-cooled engines by sludge or carbonaceous matter in the ring grooves, there is another type of ring-sticking which occurs in engines running at high piston temperatures, particularly high output, air-cooled aircraft and two-stroke engines. There is some evidence that this type of ring-sticking, which rapidly leads to piston-burning or seizure, is due to different factors from those which produce ring-sticking in low-temperature cylinders, for example, an oil which performs satisfactorily in a high-temperature gasoline engine may give trouble in a low-temperature engine and vice versa. The difference between the two classes of ring-sticking is also illustrated by the case of a certain high-speed compression-ignition engine, which is prone to ring-sticking owing to accumulation of sludge in the ring grooves. This engine runs satisfactorily only on oils which are known to have a low sludge-forming tendency and pronounced ring-sticking properties in high-temperature gasoline engines.

Very little experimental work on high-temperature ring-sticking has been published, although, in view of the great importance of the question in connexion with aircraft, a great deal has undoubtedly been done. Heron [27, 1930] in 1930 gave the results of some experiments carried out by the U.S. Army Air Corps in a small single-cylinder engine. As a result of their own observations and also those of others on high-temperature engines, during the last few years, the authors have arrived at the following general conclusions, which, incidentally, form the basis for the statement that ring-sticking at high temperatures arises from causes other than those promoting sticking at low temperatures.

(1) In addition to piston temperatures, a considerable number of factors, not necessarily connected with the lubricant, affect ring-sticking. Amongst these are piston-ring side-clearance, accuracy of finish of the plane surfaces

of the rings, and intensity of detonation, which may operate by increasing the piston temperatures locally. There is also some reason to think that the metals of the piston, rings, and cylinder have some effect.

(2) Ring-sticking is not controlled by the carbonizing or sludge-forming tendency of an oil.

(3) The general oxidation stability of oils does not appear to have a very strong influence on their ring-sticking performance.

(4) An increase in the rate of oil supply to the piston frequently delays ring-sticking.

(5) An increase in the degree of refining of an oil may have an adverse effect on its ring-sticking behaviour.

(6) The addition of fatty material to mineral oils generally promotes ring-sticking, but the effect of small proportions of fatty oil, e.g. 5%, may, in some instances, be largely counteracted by blending with suitable mineral oils, of types which are not too highly refined.

The observations mentioned under (4), (5), and (6) suggest that the material responsible for ring-sticking at high temperatures is a gummy substance soluble to a different extent in various types of oil. Over-refining of a mineral oil presumably reduces its capacity for dissolving the gum. The fact that even the most stable oils may give rise to ring-sticking indicates that such oils may form gums, just as they produce carbon and sludge-forming substances when submitted to the destructive conditions of the combustion space.

The above picture of the ring-sticking process admittedly rests on limited experimental evidence, and a great deal of work remains to be done. For the present the solution to the problem, as far as the lubricant is concerned, seems to be in the correct selection of the components of the oil. The possibilities of preventing ring-sticking by the addition of oil 'dopes' containing organic material, which inevitably decomposes in the engine, seem very limited.

The gummy substances, responsible for ring-sticking, do not appear to have been isolated. It is possible that they are similar to the alcohol-soluble 'varnish' previously mentioned. The difficulty of obtaining the gums is due to the fact that, when ring-sticking actually occurs, the gummy materials are generally carbonized by the high local temperatures.

Lubricating Quality, Oiliness, and Friction

The effects due to the decomposition of lubricating oils in use, and also those of the viscosity of lubricants on engine-starting and on rate of oil consumption, are dealt with elsewhere. Some consideration must now be given to the lubricating quality of oils in connexion with their use in internal-combustion engines.

The property of lubricants known as oiliness has received a great deal of study and its effects have been demonstrated in friction machines and other pieces of laboratory apparatus, in which the reduction in the coefficient of static or breakaway friction due to oiliness may be measured. Oiliness depends upon the chemical composition of a lubricant; it is possessed in a marked degree by animal and vegetable oils which are superior to mineral oils in this respect. The differences in oiliness between mineral oils of varying origin and degree of refining are relatively small; but the addition of a small proportion of a fatty to a mineral oil produces a lubricant possessing a degree of oiliness comparable with that of the fatty oil alone.

Although the effect of oiliness in reducing friction is quite definite under static conditions and even during actual running in certain machines and types of reduction gear in which, owing to high bearing pressures and sliding contact, the conditions favour extrusion of the lubricant, the manifestation of the results of oiliness in engines is much less definite. Since conditions of boundary lubricating occur only momentarily, if at all, in engines [52, 1934; 58, 1930], the effect of oiliness on friction during running seems to be negligible [43, 1927; 66, 1928; 5, 1935], and it has even been observed by the authors [58, 1930] that some blends of mineral and fatty oils produced a higher starting-torque than did a mineral oil of the same viscosity. In rare cases it is noticed that valve-operating mechanism which, owing to deficient design, is inadequately lubricated, wears less rapidly with a compounded than with a pure mineral oil. Another instance of the advantageous use of fatty oil is in the running in of pistons [52, 1934], particularly in steel cylinders. In this case better results seem to be obtained with castor oil than with mixtures of fatty and mineral oils, so that the effect may be one not of oiliness alone but of some chemical action of the castor oil on the metals whereby it acts as a very mild lapping or grinding material.

The use of a lubricant possessing high oiliness is sometimes thought to provide a margin of safety in case of temporary failure of oil supply. There does not appear to be any experimental support for this opinion, and, in the authors' experience, the length of time which elapses between failure of oil supply and piston seizure is more affected by the involatility than by the oiliness of the lubricant.

The great majority of the world's internal-combustion engines are lubricated with mineral oils. The question whether a particular blend of fatty and mineral oil has sufficient advantages in performance to counteract any increased tendency to gumming and carbonization due to the fatty oil can, at present, be decided only by engine trials.

The effect of the viscosity of an oil on its performance is better understood than that of oiliness. Reference has already been made to the influence of viscosity on starting and rate of oil consumption. The frictional losses in engine bearings are a function of the oil viscosity, as would be expected from the hydrodynamic theory of lubrication, and it therefore follows that oils of the lowest viscosity consistent with satisfactory lubrication and oil consumption should be applied. The minimum viscosity necessary to ensure adequate bearing lubrication naturally varies somewhat according to the particular engine, bearing pressures, and speeds, but there is some experimental evidence [59, 1933], in addition to that mentioned in regard to the effects of fuel dilution, to show that light machine oils, of about 8 centipoises viscosity (about 35–45 sec. Redwood or Saybolt) at cylinder-wall temperatures, give adequate lubrication. At present even thinner lubricants, which are equivalent to heavy spindle oils, are being recommended and used in the U.S.A. for automobile lubrication to ensure easy starting in winter.

An increase in the viscosity of the lubricant produces an increase in the frictional losses in a bearing, and hence a rise in bearing temperatures. Generally speaking, the temperature of oil in a crankcase increases with engine speed, but is not greatly affected by variations in power output in a given engine [56, 1931]. Whether the crankcase oil temperature rises or falls with the viscosity of the lubricant depends upon engine design and the extent to which the oil is thrown to the underside of the pistons. In radial aircraft engines oil temperatures are higher with low than with high viscosity oils owing to the increased rate of circulation of oil to the pistons with reduction in the viscosity of the lubricant. At the other extreme Doman [18, 1932], working with an air-cooled, six-cylinder in-line engine on the bench, found that crankcase oil temperatures were almost as high when the engine was motored as when it was firing. It seems evident that in this particular engine very little piston-cooling is done by the lubricant. C. G. Williams [63, 1932] has conclusively shown that oil temperatures are much more effectively reduced by passing cool air through the crankcase than by increasing the rate of circulation of the lubricating oil. This result is not surprising when it is realized that an increase in the rate of oil circulation generally leads to a greater rate of oil supply to the piston.

Although low viscosity is preferable to high viscosity in crankcase oils from the point of view of friction, engines commonly run with greater noise as the viscosity of the oil is reduced.

Reference has been made to oil volatility in connexion with the consumption of lubricating oil. There is no doubt that air-cooled gasoline engines may be satisfactorily lubricated by distillate oils [58, 1930] of suitable viscosity. When the cylinder-wall temperatures exceed 300° C., the presence of some residual oil, i.e. bright stock, in the lubricant seems desirable to prevent 'drying up'. In the case of 4-stroke engines, 20 or 30% of residual oil in the lubricant is generally adequate; but for 2-stroke air-cooled engines higher proportions may be necessary. Owing to the lower average cylinder temperatures involved, residual lubricants are not essential constituents of the lubricants of most types of compression-ignition engine.

Oil Consumption

The amount of lubricating oil consumed by an internal-combustion engine is normally in the region of 1–5% by volume of the liquid fuel consumption.

In the majority of engines of the trunk-piston type considerably more oil passes the piston than is required for lubrication purposes. This state of affairs is objectionable from two aspects: it causes an unnecessarily high rate of oil consumption and hastens the deterioration of the remaining oil in the crankcase. The simultaneous increase in oil consumption and oil deterioration, including sludge formation, which has already been described, follows from the fact that both are effects of the same cause, namely, enhanced rate of circulation or interchange of oil between the crankcase and combustion space.

The minimum amount of oil needed to give adequate lubrication and to prevent excessive wear of the piston rings and cylinder is obviously directly dependent upon the rate at which the lubricant is pumped into the combustion space and consumed. In trunk-piston engines, in which the oil is thrown to the piston from the big-end of the connecting-rod, the lowest attainable rate of oil consumption, without incidence of undue wear, will be considerably less than the rate of supply of oil to the piston and cylinder walls. The lowest rates of oil consumption obtained in such engines are chiefly of interest as showing how far the pumping of oil past the piston may be reduced below what is considered normal. For example, Nutt [49, 1933] quotes the case of an aircraft engine having an oil consumption, at full throttle, equal to only 0·4% by volume of the fuel used. Pye, on page 120 of his book [52, 1934], mentions a similarly low rate of oil consumption in another type of aero-engine. Williams [64, 1933] has also shown that the rate of oil consumption may, under certain conditions, be reduced to about one-tenth of that normally expected. In an engine fitted with a crosshead and guide and having a direct oil feed to the lower part of the cylinder walls, it is possible to control and measure the amount of oil which reaches the piston and cylinder. With a gasoline engine of this type, in which the crosshead and guide were designed to prevent leakage of oil from the crankcase to the piston, the authors have found that the minimum permissible rate of oil feed to the cylinder, at an engine speed of 600 r.p.m., was 0·25% of the fuel consumption.

In general, the rate of consumption depends much less upon the characteristics of the lubricant than upon the mechanical conditions of use, such as engine design, running conditions, and the state of the engine [22, 1933; 46, 1931; 50, 1931–2; 54, 1922; 20*a*, 1935]. The most important property of the oil in regard to consumption is undoubtedly its viscosity at each temperature prevailing in the crankcase, oil pipes, bearings, in the piston-ring grooves, and on the cylinder walls. The rate of movement and circulation of the oil at these points increases as the viscosity falls, and upon the rapidity of circulation depends the rate at which the oil is offered to the combustion spaces for consumption. Under service conditions, the loss by leakage through crankcase breathers, faulty joints, or defective glands or oil-throwers sometimes accounts for a considerable proportion of the total oil consumption. Loss of oil by leakage and by changing of crankcase oil do not call for consideration in this article, although it is important that such losses should be allowed for in experiments on engine-oil consumption, i.e. consumption of oil which passes the pistons and valve guides.

A considerable amount of experimental work, both on the road and the bench, has been published to show the rapid increase in the rate of oil consumption with speed [22, 1933; 46, 1931; 35, 1931; 33, 1931; 49, 1933]. The actual variation in the oil consumption naturally depends greatly upon the engine. Graves [22, 1933] refers to a series of road tests in which oil consumptions at 30 and 55 m.p.h. were compared in a number of engines. The ratio of the rate of consumption at the high to that at the low speed varied from 2·3 to 19·8 according to the car.

Although the rate of oil consumption tends to fall as the viscosity of the lubricant increases, Mougey [46, 1931] and others [22, 1933; 54, 1922] have found that when the viscosity exceeds a certain limit, the consumption in some engines rises as the viscosity increases.

There is a certain amount of evidence that oil consumption may increase with the volatility of the lubricating oil [21, 1926; 22, 1933; 61, 1931; 16*a* 1935], volatility being assessed by means of a vacuum distillation curve or by the percentage of low viscosity distillate in an oil blend. On the other hand, differences in oil volatility frequently produce no effect on oil consumption. It is often impossible to separate the effects of viscosity from those of oil volatility when studying oil consumption, owing to the difficulty of changing the volatility of an oil blend without altering its viscosity-temperature curve. In the authors' experience the effect of oil volatility on consumption is negligible in comparison with the influence of engine conditions and of the viscosity of the lubricant. In those cases in which differences between oils in regard to rate of consumption may be ascribed to differences in volatility it is generally found that the oil consumption is low, i.e. less than 2% of the fuel consumption.

The use of flash-point as a measure of relative volatility of lubricating oils is objectionable. Flash-point is greatly influenced by the presence of small proportions of low boiling-point constituents in an oil. For example, the addition of a small percentage of kerosine to a lubricant may produce a big drop in the flash-point without any appreciable effect on the rate of consumption of the oil in an engine.

Low-temperature Performance of Lubricating Oils

Considered from the point of view of engine performance at low temperatures, the properties of lubricating oils are chiefly important in regard to their effects on ease of starting. When a start has been obtained it is necessary that the oil should not offer so great a resistance to circulation that the pump is incapable of delivering it to the bearings at the normal pressure. The highest oil viscosity compatible with proper delivery of oil to the bearings varies with the nature of the pump and particularly with the cross-section of the oil channels leading to the pump. In these channels the oil moves only under the influence of atmospheric pressure and gravity. The viscosity of the oil obviously falls rapidly as it begins to circulate and as the engine warms up.

If the conditions of lubrication of a cold engine were of the 'boundary' type, starting-torque, neglecting the churning of oil in the gear-box, would be independent of the viscosity of the crankcase oil. There is, however, considerable evidence [62, 1928; 58, 1930; 23, 1934; 35, 1931; 8, 1930] that, in accordance with the hydrodynamics of fluid lubrication, the torque required to rotate a given engine in the cold depends principally upon the viscosity of the lubricant. The measurement of the viscosity of lubricating oils at low temperatures presents difficulties in the case of many oils which exhibit a marked tendency to become plastic solids [4, 1928; 62, 1928] as the temperature approaches that of the pour- or setting-point. This phenomenon is caused by the presence of waxy and other substances of high melting-point which tend to form structures as the temperature falls. The effect of these structures may be explored by carrying out the viscosity determinations at varying rates of shear and oil flow (i.e. by using different pressure falls in the viscometer), since the plasticity effects diminish as the rate of shear is increased. In the engine the rigidity effects are not so marked as in the viscometer, owing to the high rates of shear and to mechanical agitation, which break the wax structures, and oils commonly behave as fluids at temperatures considerably below the pour-point. It may be mentioned, in this connexion, that the rate of shear of an oil, under conditions of low-temperature viscosity determination in a capillary tube, is of the order of 10 or 100 radians per sec., while the rate of shear in a plain bearing with a 2-in. diameter journal rotating at 100 r.p.m. is 1,000 radians per sec., even when the bearing clearance is as large as 0·01 in. The rate of shear increases directly with the relative velocity of the bearing elements, and inversely as the bearing clearance.

A number of investigators have examined the behaviour of lubricating oils in actual engines at low temperatures both from the point of view of ease of starting, engine friction, and pumpability of the oil. 'Breakaway' torque, i.e. the torque required to start a cold engine turning, is more difficult to measure accurately than are readings at a steady speed, but certain investigators [36, 1931; 7, 1935] who have determined breakaway torque readings at temperatures from $-1°$ C. to $-18°$ C. find that it is about twice that required to maintain steady rotation of the crankshaft.

Most authors who have described friction and motoring-torque experiments with engines at low temperatures have found that the effect of pour-point is unimportant in comparison with that of viscosity in relation to the torque readings.

The low-temperature viscosities of oils of low pour-point may be measured without difficulty in capillary viscometers. Before the pour-point temperature is attained, the viscosity of this type of oil usually reaches a figure of such magnitude that measurements at lower temperatures are not required for comparison with engine observations. To obtain the effective viscosities of waxy oils at temperatures around and below their pour-point it is necessary either to carry out the measurements at a high rate of shear or to extrapolate the viscosity-temperature curve determined over the normal temperature range between 100° and 20° C. Extrapolation is obviously not satisfactory unless the viscosity-temperature curve is linear, and hence some workers [4, 1928; 62, 1928; 10, 1931] have used the special scales of logarithmic type, such as those of MacCoull [40, 1921], Herschel [28, 1926], Vogel [60, 1921], and the A.S.T.M. [2, 1932], in which viscosity-temperature curves appear as straight lines.

Although most of the factors affecting the behaviour of lubricants in engines at low temperatures appear to have been known by the year 1925 [23, 1934], the first systematic survey of the subject was made in 1928 by Wilkin, Oak, and Barnard [62, 1928]. These authors also described their own investigations which showed that the turning-torque of a cold engine is controlled by the viscosity of the oil. More recently it has been found that the torque is proportional to the square root of the viscosity [58, 1930; 7, 1935].

Blackwood and Rickles [10, 1931] carried out a series of starting tests in a cold chamber on a number of American motor-cars manufactured in the years 1930–1. They found very considerable differences in the performance of the engines. For example, some engines would start at a cranking speed as low as 20 r.p.m., whilst others required to be turning at over 60 r.p.m. to effect a start. Although one engine started with a lubricant having a viscosity as high as 85,000 Saybolt Universal (roughly 15,000 centipoises), the maximum viscosity which allowed starting in the majority was between 20,000 and 40,000 Saybolt (roughly 3,000–6,000 centipoises). Two engines would not start when the viscosity of the oil exceeded 9,000 Saybolt (about 1,500 centipoises). It is obvious that the maximum viscosity of the lubricant on which starting can be obtained must depend to a great extent on the performance of the starter battery and motor. Blackwood and Rickles used the individual starting equipment belonging to each car. In later work, Blackwood [9, 1935] found that the cranking torque rises with fall in temperature, even when the oil viscosity is kept constant by changing the lubricant, probably owing to the reduction of bearing clearances as the temperature falls.

Barrington and Lutwyche [7, 1935] find that very few British cars will start satisfactorily at $-1°$ C. unless they are cranked at a speed of at least 60 r.p.m. These authors have also determined the cranking torque due to the various moving parts of a particular engine.

The behaviour of lubricants when pumped at low temperatures has been examined by Larson [35, 1931], using the oil pump of a Ford engine. The rates of delivery of oil were measured at various temperatures and plotted against viscosity. Smooth curves were obtained which, for oils with pour-points of 0° F. and higher, extended down to temperatures as much as 10° F. below the pour-point. Although the rates of delivery of the oils below their pour-points indicated the absence of rigidity effects, it was observed [35, 1931; 39, 1933] that even at temperatures above the pour-point the presence of wax reduced the rate of delivery, so that, in effect, the wax raises the viscosity of the oil for pumping purposes. In such cases the measured or extrapolated viscosities at a given rate of pump delivery vary with the nature of the oil, i.e. with the wax content.

The pour-point as well as the viscosity of a lubricating oil is of significance in regard to the flow of oil to the suction side of the oil pump [62, 1928; 39, 1933], since at temperatures below the pour-point the formation of wax structures tends to hinder the free flowing of the oil. The pour-point of an oil generally falls in service, partly owing to the presence of fuel diluent, so that these considerations are more important with fresh than with used oil.

Wear

The determination of piston and cylinder wear by diametral measurements cannot be employed in conjunction with short running periods, of about 10–50 hours, unless special methods [64, 1933] of measurement are applied to deal with minute dimensional changes.

The loss in weight of piston rings is frequently used for estimating wear. Results may be obtained by this method in tests of a few hours' duration, but it is essential to check the repeatability of the results, since the rate of ring wear may vary very greatly in some engines, probably owing to movement of the rings in the plane of the grooves, without any apparent change in running conditions. Furthermore, it is unsafe to assume that cylinder wear is proportional to piston-ring wear without verification in any particular combination of materials.

Measurement of wear is possible in some cases by determination of the amount of iron and other bearing metals in the lubricating oil [32, 1933; 44, 1935; 20*a*, 30*a*, 1935]. In trunk-piston engines this method involves the complete removal of the crankcase contents, an operation which is generally difficult to perform satisfactorily. Iron analysis of small portions of the oil withdrawn during running of the engine does not usually give reliable wear data owing to the tendency of the ash constituents of the oil to settle out. When it is possible to collect all the used oil draining down from the piston and cylinder [12, 1932], as in engines with crosshead pistons, analysis of the oil samples taken during equal time intervals enables an estimate to be made of the total cylinder, piston, and ring wear to be made. It is preferable to determine the metal content of the oil rather than the total ash, since the dust or silica present may vary somewhat without a corresponding change in the quantity of metal from the wearing surfaces. It should be borne in mind that wear measurements based on the analysis of oil for metal content involve the assumption that the amount of metal remaining in the oil is, in a given engine, a constant proportion of the total quantity worn from the metal surfaces; or, in other words, the loss of metal in carbon deposits in the combustion space or through the exhaust ports is a constant proportion of the total metallic wear. This assumption is, in the authors' experience, reasonably sound.

Until the last few years it was generally assumed that wear was normally caused by abrasive dust or by the occurrence of metallic contact of the bearing elements. It has, of course, been shown that the presence of excessive amounts of dust [32, 1933; 31, 1930; 64, 1933] in an engine increases the rate of wear, but the possibility of metallic contact in a properly designed and lubricated bearing, except perhaps between piston rings and cylinder near top dead centre on the firing stroke, seems rather remote. In 1932 Ricardo [53, 1933] gave reasons for thinking that wear is not entirely due to abrasion and suggested that metallic corrosion by products of combustion might be one of the major causes of cylinder and piston wear. Strong support to the corrosion theory of wear was given by the important experiments on gasoline engines on the bench, described by Williams [64, 1933; 65, 1934], and carried out for the Research Committee of the Institution of Automobile Engineers. These articles, which deal with the most important piece of work on cylinder wear in internal-combustion engines which has yet been published, should be studied by all who are concerned with engine wear. After showing that reduction of the rate of oil supply to the bearings to 1/100th of the normal, increasing the cylinder-wall temperature from 125° to 265° C., and raising the B.M.E.P. from 60 to 100 lb. per sq. in., had no appreciable effect on wear in the single-cylinder test engines, Williams demonstrates that rate of cylinder and ring wear increases rapidly as the cylinder-wall temperature falls below 90° C. At these low temperatures the wear is reduced by increasing the oil supply to the cylinder. Further experiments established that the high wear at low temperatures is due to the corrosive action on the cylinder walls of condensed water assisted by carbon dioxide and sulphur oxides. It is evident that for cylinder and piston rings, metals possessing a high resistance to corrosion may be more satisfactory for wear reduction than those selected for other properties, especially in engines working principally at low cylinder temperatures. At the same time, the results show the necessity for reducing the 'warming-up' period and the undesirability of keeping cylinder-wall temperatures below about 90° C., at any rate near the upper end of the bore where the maximum cylinder wear almost always occurs. In general it is not possible to determine how much of the total wear in an engine is due to corrosion on the one hand, and to abrasion on the other hand. Data on the running conditions and temperatures may, however, make it possible to decide whether corrosion-wear is likely to be important.

REFERENCES

1. Arveson, M. H. *Ind. Eng. Chem.* **24**, 71 (1932), and **26**, 628 (1934).
2. *A.S.T.M. Proc.* **32**, part i, 772 (1932). A.S.T.M. designation of chart D. 341–2 T.
3. Bahlke, W. H., Barnard, D. P., Eisinger, J. O., and Fitz-Simmons, O. *S.A.E. Trans.* **26**, 373 (1931).
4. Barnard, D. P. Round Table Discussion on Lubrication. *Ind. Eng. Chem.* **20**, 843 (1928).
5. Barnard, D. P. and E. R. *Refiner*, **14**, 324 (June 1935).
6. Barnard, D. P., Barnard, E. R., Rogers, T. H., Shoemaker, B. H., and Wilkin, R. E. *S.A.E. Trans.* **29**, 107 (1934).
7. Barrington, R., and Lutwyche, J. L. *J. Inst. Auto. Engrs.* (London), **3**, no. 8, p. 15 (1935).
8. Becker, A. E., and Bauer, W. C. *Oil and Gas J.* **28**, no. 40, pp. 46, 155 (1930).
9. Blackwood, A. J. *J.S.A.E.* **36**, 70 (1935).
10. Blackwood, A. J., and Rickles, N. H. *S.A.E. Trans.* **26**, 327 (1931).
11. Boerlage, G. D. *J.I.P.T.* **16**, 678 (1930).
12. Boerlage, G. D., and Gravesteyn, B. J. J. *The Motor Ship* (London), August 1932.
13. Bouman, C. A. *Proc. World Petr. Cong.* London, **2**, 248 (1933).

14. Brooks, D. B. *S.A.E. Trans.* **21**, part i, 21 (1926).

15. Clayden, A. L. *S.A.E. Trans.* **19**, part ii, 58 (1924).

16. —— *A.S.T.M. Symposium on Motor Lubricants*, New York, 8 March 1933, p. 101.

16*a*. Davis, L. L., and Best, R. D. *Nat. Petr. News*, **27**, 70 (26 June 1935).

17. Dietrich, M. A. *A.S.T.M. Symposium on Motor Lubricants*, New York, 8 March 1933, p. 57.

18. Doman, C. T. *Oil and Gas J.* **30**, 95 (31 March 1932).

19. Ehlers, C. *Petr. Z.* 1930, no. 15. Motorenbetrieb und Maschinen-Schmierung, ibid. 1931, no. 49; 1932, no. 19.

20. Eisinger, J. O. *S.A.E. Trans.* **19**, part ii, 1 (1924).

20*a*. Everett, H. A., and Stewart, F. C. Performance Tests of Lubricating Oils in Automobile Engines. Pennsylvania State College Bulletin, Engineering Experimental Station, Series no. 44 (27 May 1935), *Automotive Industries*, **73**, 363 (1935).

21. Gavin, M. J., and Wade, G. *U.S. Bureau of Mines, Technical Paper*, no. 387 (1926).

22. Graves, W. H. *A.S.T.M. Symposium on Motor Lubricants*, New York, 8 March 1933, p. 85.

23. Graves, W. H., Mougey, H. C., and Upham, E. W. *S.A.E. Trans.* **29**, 238 (1934).

24. Gruse, W. A. *A.S.T.M. Symposium on Motor Lubricants*, New York, 8 March 1933, p. 7; *Proc. World Petr. Cong.* London, **2**, 441 (1933).

25. Haslam, R. T., and Bauer, W. C. *S.A.E. Trans.* **26**, 418 (1931).

26. Haslam, R. T., Russell, R. P., and Asbury, W. C. *Proc. World Petr. Cong.* London, **2**, 302 (1933).

27. Heron, S. D. *Amer. Soc. Mech. Eng. Trans.* **52**, A.E.R. 233 (1930).

28. Herschel, W. H. *Oil and Gas J.* **25**, 146 (2 Dec. 1926).

29. Hoffman, A. H. *Univ. of California, Agricultural Experiment Station, Berkeley, Calif., Bulletin* 499 (Oct. 1930).

30. Holde, D. *Kohlenwasserstofföle und Fette*, 6th (German) edit. (Julius Springer, Berlin), 184 (1924).

30*a*. Keller, C. M. *Automotive Industries*, **72**, 484 (1935).

31. König, K. *Automobiltechnische Z.* 1930, p. 965.

32. Langdon, H. H. *State College of Washington, U.S.A., Engineering Bulletin*, no. 42, March 1933.

33. Larson, C. M. *A.S.T.M. Symposium on Motor Lubricants*, New York, 8 March 1933, p. 110.

34. —— Ibid. p. 77.

35. —— *J.S.A.E.* **29**, 210 (1931).

36. Lederer, E. R., and Zublin, E. W. *Nat. Petr. News*, **23**, 37 (30 Sept. 1931), and 27 (7 Oct. 1931).

37. Levi, R. *Petr. Z.* 1932, no. 15, Motorenbetrieb, p. 2.

38. Livingstone, C. J., and Gruse, W. A. *Ind. Eng. Chem.* **21**, 904 (1929).

38*a*. Maillard, A., Acker, A., and Rengade, F. *Annales des Comb. Liquides*, 945 (Sept.–Oct. 1936).

39. McCloud, J. L. *A.S.T.M. Symposium on Motor Lubricants*, New York, 8 March 1933, p. 27.

40. MacCoull, N. *Lubrication*, **7**, 5, June 1921 (pub. by The Texas Co.).

41. Marley, S. P., and Gruse, W. A. *Ind. Eng. Chem.* **24**, 1298 (1932).

42. Marley, S. P., Livingstone, C. J., and Gruse, W. A. *J.S.A.E.* **18**, 607 (1926).

43. Marshall, A. G., and Barton, C. H. *J.S.C.I.* **46**, 130 T (1927); *Engineering*, **123**, 435 (1927).

44. Merrill, D. R., Moore, C. C., Jr., and Bray, U. B. *Refiner*, **14**, 313 (June 1935).

45. Meston, A. F. *Ind. Eng. Chem.* **19**, 312 (1927).

46. Mougey, H. C. *J.S.A.E.* **29**, 200 (1931).

47. —— *Ind. Eng. Chem.* **20**, 18 (1928).

48. —— *Automotive Industries*, **70**, 334 (1934).

49. Nutt, A. *A.S.T.M. Symposium on Motor Lubricants*, New York, 8 March 1933, p. 114.

50. Ottaway, E. C. *Proc. Inst. Aut. Eng.* (London), **26**, 150 (1931–2).

51. Philoppovich, A. von. *Ber. D.V.L.* (Berlin), **6**, 36 (1933).

52. Pye, D. R. *The Internal Combustion Engine*, **2**, chap. v (Oxford Univ. Press, 1934).

53. Ricardo, H. R. *Proc. Inst. Aut. Eng.* (London), **27**, 434 (1932–3); *Soc. Chem. Ind.* (London), *Proc. Chem. Eng.*, Group XV, 31 (1933).

54. Round, G. A. *J.S.A.E.* **10**, 509 (1922).

55. Sloane, R. G., and Winning, C. *Ind. Eng. Chem.* **23**, 673 (1931).

56. Sparrow, S. W. *Automotive Industries*, **64**, 916 (1931).

57. Stewart, J. P., and Risk, T. H. *J.S.A.E.* **33**, 42 (Oct. 1933).

58. Thornycroft, O., and Barton, C. H. *Aircraft Engineering*, **2**, 36, 109 (1930).

59. Upham, E. W. *A.S.T.M. Symposium on Motor Lubricants*, New York, 8 March 1933, p. 38.

60. Vogel, H. *Physik. Z.* **22**, 645 (1921).

61. Wade, G., and Foster, A. L. *U.S. Bureau of Mines, Tech. Paper* no. 500 (1931).

62. Wilkin, R. E., Oak, P. T., and Barnard, D. P. *J.S.A.E.* **22**, 213 (Feb. 1928).

63. Williams, C. G. *Engineering*, **133**, 464 and 523 (1932).

64. —— *J. Inst. Auto. Engrs.* (London), June 1933, p. 73; *The Engineer*, **155**, 634, 660 (1933).

65. —— *J. Inst. Auto. Engrs.* (London), **2**, 19 (Aug., Sept. 1934); *Engineering*, **138**, 103, 182 (1934).

66. Wilson, R. E., and Barnard, D. P. *Proc. A.S.T.M.* **28**, part ii, 684 (1928).

67. Wilson, R. E., and Wilkin, R. E. *S.A.E. Trans.* **21**, part i, 81 (1926); *Ind. Eng. Chem.* **18**, 486 (1926).

THE LUBRICATION OF INTERNAL-COMBUSTION ENGINES

By D. R. PYE, M.A., Sc.D., F.R.S., F.R.Ae.S., M.I.Mech.E.

Director of Research, Air Ministry.

It is inevitable that among the diversity of types included within the general class of internal-combustion engines there should be many problems of lubrication which cannot be covered in a general article. What follows is based chiefly upon experience with engines of the smaller, high-speed types used in road and air transport, but much of it may be read as applying equally to engines of larger cylinder size and lower rotational speeds. It is the mean piston speed which is important in cylinder lubrication, and the limits of this do not differ widely with engine size.

The essential difficulty of the lubrication problem in the internal-combustion engine is that the oil has to serve a dual purpose. In the cylinders it must maintain its lubricating properties between metal surfaces which may be in the temperature range 150°–200° C., and must also withstand being swept by the cylinder gases at temperatures of 1,000°–2,000° C. Chemical stability is therefore a prime consideration, both against oxidation and 'cracking' of the oil molecules. In the bearings and gears, on the other hand, chemical stability is of far less importance and might well be sacrificed in favour of the elusive property of oiliness, known to be associated with polar, i.e. chemically active, molecules (see Introductory article to this section, p. 2558). The ideal, which would be to employ separate oil supplies for the cylinders and for the bearings and gears, is for the most part impracticable, and in very high duty engines development has taken the line of employing mineral oils for their greater chemical stability, and of meeting any deficiency they may show under conditions of boundary lubrication by more perfect mechanical design, to minimize local concentrations of stress. By the more perfect forming of gear teeth, for example, excessive local pressures can be avoided and gears can be made to function satisfactorily with a mineral oil, which formerly were liable to abrasion of the tooth surfaces. Under these severe conditions castor oil shows a remarkable superiority over other lubricants which has nothing to do with its high viscosity. The property of 'oiliness', possessed by castor and other 'fatty' oils to an exceptional degree, depends upon the power of certain types of oil molecules to arrange themselves in a definite orderly manner when forming primary films on a metal surface (see Introductory article to this section, p. 2558). The film is said to be 'adsorbed' on the surface of the metal, and it adheres so powerfully as to be removable only with the greatest difficulty.

The beneficial effect of castor oil upon lubricated surfaces, and its persistence after removal of the oil supply, has led to the practice of 'running-in' new engines for several hours upon castor oil, by which time the surfaces have become thoroughly impregnated, and thereafter turning over to mineral oil for the rest of the engine's life. The unsatisfactory qualities of the castor as a piston lubricant, by reason of its propensity to oxidation and gum formation in a hot cylinder, would not become evident until after a hundred hours or more of running, so that its use for a few hours with new engines allows some of its admittedly superior qualities for bearings and gears to be retained without subsequent danger from the sticking of piston rings.

The undoubted benefit to be derived from preliminary running on castor oil raises questions of the importance or otherwise of viscosity, and to what extent conditions approaching those of boundary lubrication occur during the normal working of an engine. All the evidence goes to show that in normal running the friction of an internal-combustion engine is almost wholly of the fluid type. Between the cylinder wall and the outer surface of the piston rings the condition of boundary lubrication may prevail to some extent, more especially during the early part of the expansion stroke when the high gas pressure, getting behind the rings, may largely increase the normal pressure between them and the cylinder walls. To a lesser degree it may happen also at the end of the stroke, when the piston velocity drops to zero. During the central part of the stroke the high piston speed enables the ring to ride-up on an oil film of appreciable thickness, and in these conditions the friction force is largely unaffected by the surface condition of the metal and of the oil. Between the piston skirt and the cylinder wall the conditions may approach those of boundary lubrication over a small part of the circumference, on the side which is subject to the thrust of the connecting-rod; but round the rest of the circumference they will everywhere be those giving viscous friction.

That an engine as a whole exhibits the phenomena of fluid rather that solid friction has been proved by experiments upon the rate of deceleration of a freely running engine when the power is cut off, for the power absorbed has been shown to be proportional nearly to the square of the speed. There is also the point that the friction losses observed when motoring engines, while they are still hot after running under power, are found to correspond closely to the viscosity of the oil used, and to show none of the large differences between lubricants which can be demonstrated under conditions of boundary friction. For example, an engine lubricated with a fatty oil, which showed a coefficient of 0·03 under boundary conditions, showed a higher friction loss than when lubricated with a mineral oil of which the boundary friction coefficient was no less than three times that of the fatty oil. Furthermore, if a rough estimate is made of the mechanical efficiency and the heat generated in the bearings of an engine, using boundary friction coefficients, it will be found that the mechanical efficiency is quite impossibly low, and that the heat generated in the bearings must inevitably lead to seizure. We may conclude, therefore, quite definitely, that by far the major portion of the friction loss in an engine is by fluid friction, with boundary conditions occurring only from time to time between the 'high points' of two bearing surfaces, and possibly between the cylinder and piston rings near the two ends of the stroke. Although the friction loss during normal running depends upon the viscosity of the lubricant, the safety of the engine from seizure, on the other hand, will by no means be independent of the characteristics of its lubricant under boundary conditions.

On the question of the part played by the viscosity of an oil, and of its importance, there are many opinions but there is little certainty. It is customary to specify a minimum viscosity for an oil at a certain temperature, and when engines have been designed to work with oil of a certain viscosity it is not safe to change that viscosity without simultaneous attention to bearing clearances, piston-ring design, and the working oil pressure which is maintained by the relief valve. A simple lowering of the viscosity of the oil used would allow of a more rapid flow through the shaft bearings, and better cooling; but it would mean also that more oil per revolution would be thrown on to the cylinder walls and this would lead to an excessive rate of oil consumption unless provision against it were made by redesign of the bearings and of the piston scraper rings.

How far a high viscosity is a safeguard against lubrication failure, either at the pistons or gears, is a question to which there is no simple answer. When once the oil film has been squeezed out, and boundary lubrication has set in, with the surfaces in contact, there is no doubt at all that the viscosity of the lubricant can play no further part in preventing seizure. But seizure under these conditions will depend not only on the lubricant, but also, if the load is sufficiently severe, upon how long the condition of boundary lubrication persists. The more viscous the lubricant, the longer will it take to be squeezed out from between two surfaces, and, remembering the undulating nature of every bearing surface considered in relation to films of molecular dimensions, it is quite clear that an oil of low viscosity will in general allow longer periods of metallic contact between the high points of a bearing, for a given load per unit area. On the other hand, if the less viscous oil should give a lower coefficient of friction in boundary lubrication, the rate of heat production would be less, and seizure less imminent.

It will be seen, therefore, that although viscosity plays no part once the metal surfaces are in contact, it may yet be a safeguard against seizure through its delaying the occurrence of that contact. How far viscosity is an effective factor in maintaining the oil film depends very much on the type of surface considered. Between a cylindrical journal and its bearing it is probably of the first importance, for the eccentricity of the journal allows, indeed it induces, a constant supply of fresh oil at the point of maximum load concentration. As between a piston ring and the cylinder wall, however, it is doubtful whether viscosity can help so much to prevent the metallic contact, although here again, if one is right in thinking that boundary lubrication only sets in at the two ends of the stroke, it can be argued that it will set in sooner with a less viscous oil.

It may be, but it does not necessarily follow, that an oil of low viscosity is also more volatile than a more viscous one. If that is so, then it must increase the danger of piston seizure with the less viscous oil, for towards the end of the exhaust stroke in a 4-cycle engine the piston and rings are dependent for lubrication upon what is left upon the cylinder walls after exposure for nearly a whole revolution of the shaft to temperatures of 1,000°-2,000° C. In these circumstances the danger of a dry wall must be directly dependent on the volatility of the oil.

This scorching of the oil film on the cylinder walls during every alternate revolution (in a 4-cycle engine) cannot be without effect on the surfaces of the oil, either in the way of 'cracking' it to form unsaturated and gum-forming hydrocarbons of smaller molecular weight, or of partial oxidation when free oxygen is present in the cylinder gases. After the working stroke the altered surface film is overrun by the piston again, and some of the products of the cracking and oxidation processes find their way into the spaces around the rings near the top of the piston. In a high duty engine the piston itself may reach temperatures ranging from 250° C. at the centre to 200° C. at the periphery under normal working conditions and possibly 100° C. higher for short periods, and the association of these temperatures in the metal with an accumulation of cracked and oxidized oil off the cylinder surface prepares the way for the sticking of piston rings. This is brought about by the fatal metamorphosis of the oil into the very antithesis of a lubricant, namely into a sticky, glue-like substance, insoluble in the original oil and, in its final stages, insoluble in almost anything.

Carbon and Sludge Formation

If a clean engine is filled with clean oil and run for even a comparatively few hours at a high power-output, not only will the oil have become black, but the crankshaft and connecting-rods will, with a mineral oil, be found covered with a black surface film which when cold is quite hard and takes on a polish like varnish. After prolonged running a sticky black sludge will be found separated out from the oil at certain points, such as inside a hollow crankpin, and there will be caked carbon on the top of the piston. It may be added for later reference, moreover, that as a general rule the blackening of the oil and the production of a filthy condition in the engine is more rapid in engines of the Diesel type than in a properly adjusted petrol engine.

Clearly the blackening of the oil must be due to the presence of suspended carbon in a finely divided state: so fine that much of it cannot be removed by filtration. What causes the carbon formation, and where it is produced, will be discussed later. A further essential element in the production both of sludge and of hard carbon is the formation of gummy substances by the polymerization and partial oxidation of the oil molecules, the latter process being one which is much accelerated by the presence of a metal surface. Probably some gum formation begins at once, but the early products of oxidation are soluble in the oil itself, and an engine may run for very many hours after the oil has become perfectly black with suspended carbon without the amount of gum formed being serious or even perceptible, unless the temperatures throughout the engine are exceptionally high. If they are, decomposition and oxidation will be more rapid and the more viscous products of the process will collect, already black with carbon, in such places as piston-ring grooves, drain-holes, and in the wider parts of the oil-ways in the crankshaft where the flow is sluggish. At first the decomposition products would only show increased viscosity, but under the influence of sluggish movement and a sustained high temperature their nature gradually changes to that of something sticky or nearly solid, and quite black.

At this stage they form the *sludge* which is found collecting in oil-ways and in the drain-holes from the ring grooves in the piston. Wherever collections of sludge are constantly in contact with more oil, as inside the crankshaft and over the lower parts of the piston, it may go on gathering to itself more sludge, but it has no opportunity of getting much beyond the sticky or india-rubbery condition. Any sludge, however, which may have collected in the upper piston-ring grooves or round the top land of the piston, is subject to far more severe temperature conditions, and in an overheated engine may rapidly congeal to a hard cement in which the rings become fixed, and piston seizure is then imminent. The hard cement found round the top land and on the piston top consists very largely of carbon and, together with the similar products on the valves and cylinder heads, represents the amount of *carbonization* which has taken place.

Some carbonization there will always be, on the piston top and the walls of the combustion space, even when there is no danger at all from stuck rings; but here again the final product is the result of decomposition and partial oxidation: a high temperature acts first on the oil to form gums impregnated with carbon, and then turns these into a black solid, hard or soft, dry or oily, according to the design of the engine and the adjustment of the oil supply. Most carbon deposits have probably gone through an earlier stage when their nature was that of a not insoluble gum impregnated with soot from the combustion, although the progress to the final, hard, insoluble deposit, being continuous and yet under different conditions from point to point, it would be impossible to separate it into definite stages.

It may be objected that dry and flaky carbon may sometimes be found on the piston-top and cylinder-head surfaces with no sign of gummy or caked products. This is, indeed, the ideal to be aimed at. We can scarcely hope to avoid soot, and the consequent blackening of the oil, for reasons explained below, but so long as this is not associated with gum formation to consolidate it into fixed carbon there will be no danger to the piston, nor will the carbonization on the piston top be serious.

It has been suggested by Thornycroft and Barton [1] that the amount of carbonization with any given oil depends entirely upon the behaviour of that oil in the combustion space above the piston. Partial combustion of small droplets of oil thrown off the piston at the top of the compression stroke is put forward by these writers as the cause both of carbon and gum formation, and figures are given of the measured weight of carbon on a piston top after 50 hours running which go to show that only when the petrol-air mixture was rich did the combustion of the fuel appear to contribute to the weight of carbon collected.

Undoubtedly most of the finely divided carbon is formed on the combustion side of the piston, possibly much of the gum also, but an alternative picture of what happens, given below, according to which the soot and the gums that together make for carbonization are of separate origin, appears to fit all the facts rather more readily. Although it has been shown that oil is thrown off from a piston in a fine spray when an engine is motored at a high speed with the cylinder heads off, it must be remembered that engines can be run for long periods with so low an oil consumption as to make it almost inconceivable that oil could be sprayed from the pistons. A 12-cylinder aero-engine, for example, of bore and stroke $5 \times 5{\cdot}5$ in., has been run for 100 hours at 2,250 r.p.m. and $\frac{9}{10}$ full load with an average oil consumption of $2\frac{1}{2}$ pints per hour. A simple calculation shows that this is equivalent to just about 1 cu. mm. of oil per cylinder per rev. This oil spread over the cylinder bore would make a film 2×10^{-6} cm. thick, so that it only needs a film of this ultra-microscopic thickness to be burnt off or evaporated per stroke to leave nothing left to be thrown off by the piston.

There are good grounds for supposing that a certain amount of finely divided carbon, sufficient to produce the blackening of the oil, is derived from imperfect combustion of the fuel. Within a thin boundary layer near the comparatively cool walls (150°–200° C. at the most) it seems certain that complete combustion of the fuel-air mixture must be arrested, and some carbon thrown down. This is sufficient to explain the presence of some finely divided carbon in the cylinder-gases during every working stroke. Swept in all directions by gas movements, some of this will stick to the cylinder walls on which many of the surface molecules of the oil film, by the end of the stroke, must have been decomposed. During the exhaust stroke the sooty and half-decomposed surface of the oil is first overrun by the piston and then washed by fresh oil thrown up by the connecting-rod big-end.

This appears to be an adequate explanation of the rapid blackening of the oil in the crankcase, and in being quite independent of any gum formation it fits in with the fact that blackening of the oil can take place in a cold engine at moderate speeds, when gum formation would be negligible and the oil too viscous to be thrown off the pistons. The more rapid fouling of the oil in a Diesel engine follows naturally, for in that type the soot in the cylinder gases is sufficiently prevalent to be visible in the exhaust, at all except light loads.

There is, however, no reason to suppose that *all* the carbon produced is formed first above the pistons. The black varnish found with mineral oils on the connecting-rods and on the under sides of the pistons may very well owe its origin to oxidation of the oil at the metal surfaces where it is found. Steel and aluminium are known to be active catalysts for the oxidation of mineral oils, and the fact that a similar blackening is not found with castor oil, although the oil itself becomes no less black, suggests that the deposits obtained with mineral oil are due to local break-down of the oil. The cleanliness of the metal surfaces with castor oil is also to be associated with the acidity which accompanies the decomposition of the fatty oils (see Chemical Nature of Lubricating Oils by F. B. Thole, p. 2576). The fatty acids formed, if any moisture is present, have a faintly corrosive and hence a cleansing effect on the metal surfaces.

Turning now to the question of gum formation, a proportion of the scorched and decomposed surface film will find its way into the ring grooves of the piston during the exhaust stroke, and if allowed to remain there at a high temperature it will provide the material for a gradually stiffening black cement. The early products being soluble in the oil itself, a very ample oil supply should prevent the amount of gum formed ever becoming serious, even in a very hot engine. This has in fact been found to be the case, and it is a result which it would be difficult to reconcile with the suggested spraying of oil from the piston as what leads to gum formation; for this could then scarcely fail to become worse and worse the more oil there was to be thrown off, whereas if the gum is first formed on the cylinder walls an ample oil supply would only facilitate solution of the gum without increasing its amount.

In the crankcase the oil will be sprayed in all directions in an oxidizing atmosphere, but the temperature will rarely be above 100°–150° C., and with all except the vegetable oils the rate of oxidation at this temperature is very slight. A certain amount of the semi-oxidized products will be washed from the cylinder walls into the crankcase oil and will be ready to form sludge at any points where it can collect, but apart from the formation of the black varnish on the metal surfaces, already referred to, there seems no reason to suppose that oxidation proceeds in the crankcase to any considerable extent except on the under sides of the pistons.

For a further discussion, and some recent experimental results, on the subject of sludge formation, a paper by Barnard and others [2] may be consulted.

Carbonization in Relation to Chemical Composition

The blackening of a lubricating oil by soot formed from the fuel being, in itself, harmless, the essential factor in carbonization is the liability of an oil to form partial oxidation products of a gummy or resinous nature; and the best oil from this point of view will be the one which is most stable against oxidation or polymerization at the working temperatures.

The great difficulty in the way of correlating an oil's resistance to oxidation with its chemical composition lies in the lack of real knowledge of what the composition is. Between the broad classes of the fatty oils and the mineral oils there are wide differences of behaviour and composition, and the chemistry of the fatty oils is known with some exactness. As between different mineral oils, however, one has to be content with describing them as Pennsylvanian 'bright stock', a 'naphthenic base' oil from Russia, or an 'asphaltic base' from Venezuela, the names signifying no more than the source and the type of crude oil from which they come. The whole problem would be vastly simplified if the components of the mineral oils could be segregated from one another and if the stability of the various constituents in the presence of oxygen could be experimentally assessed. In the absence of any such analysis the mixed oils of commerce must be treated as a whole, and their reaction to oxygen must be assessed indirectly by physical tests of viscosity and kindred properties. Such physical tests have been widely used for specification purposes. They provide a fair general indication of the chemical stability of an oil, but the conditions under which oxidation takes place are very different from those in an engine, and it cannot be claimed that the behaviour of an oil in an engine as regards carbonization can be foreseen with certainty by any laboratory oxidation test so far devised.

The rate of absorption of oxygen by lubricating oils at different temperatures has been directly observed by various experimenters, one method being to enclose 1 g. of the oil in a small cylinder filled with air. The glass cylinder is rotated slowly inside an electric furnace at a known temperature, and the oxygen content of the air is measured after various intervals of time. The results are then expressed as so many milligrams of oxygen absorbed by a gram of oil in 1 hour.

Without knowledge of what happens to the absorbed oxygen, and whether the chemical changes brought about by it are not very different in different oils, the test can never be a conclusive one of an oil's behaviour in an engine. And there is evidence, moreover, that an oil which in this form of test does not readily absorb oxygen may yet show up badly in regard to carbon deposits during an engine test. The oxygen absorption test is nevertheless of some interest in the striking way it differentiates between castor oil and the mineral oils; and it is of value also as a way of showing up the catalytic action of certain metals in promoting oxygen absorption, and its prevention by inhibitors.

In Fig. 1 are given the results of tests upon castor oil and three different types of mineral oil. It is at once evident that castor oil is in a different class from the others. It readily absorbs oxygen at temperatures above 125° C. and rapidly increases in viscosity. Under the conditions of the experiment 1 g. of castor oil at 150° C. absorbed about 20 mg. of oxygen in 1 hour. None of the mineral oils absorbed oxygen appreciably below about 140° C., and even at 250° C. the Pennsylvanian bright stock after heating for an hour had only absorbed about 10 mg. of oxygen. After 3 hours heating at 250° C. the gummy and oxidized oil was still soluble in benzene without residue.

The Russian oil behaved in a very similar way, but appeared to be a little more ready to absorb oxygen at 150° C. and above, although it showed signs of better stability below that temperature. This is shown by the dotted curves on the right of Fig. 1 which show the oxygen absorption, to a more open scale, at temperatures below 140° C. There was no appreciable absorption by any of the oils except castor oil below 110° C.

The asphaltic base oil was definitely inferior to the other two mineral oils, the rate of oxygen absorption at 175° C. being about the same as that of the Pennsylvanian oil at 250° C. This difference between asphaltic oils and those of naphthenic or paraffin base is generally in accordance with experience on engines.

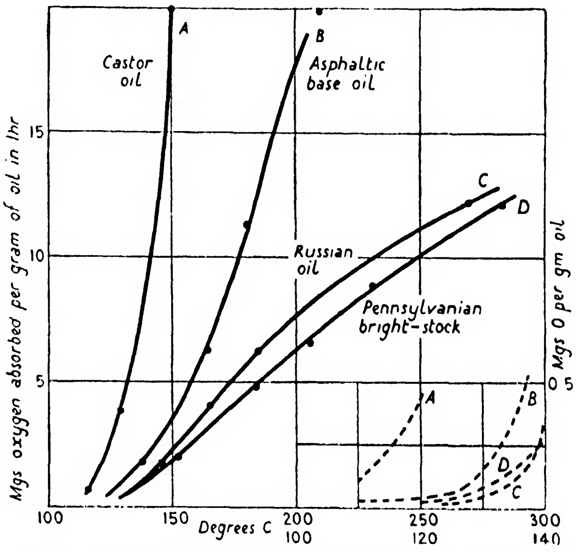


FIG. 1. Rate of absorption of oxygen by castor oil and three different mineral oils when maintained at various constant temperatures.

The presence of strips of copper, iron, and aluminium placed in the oil did not increase the rate of oxygen absorption by the mineral oils below 175° C., but tended to make the oxidized oil discoloured, thick, and insoluble in benzene. From the point of view of piston-ring gumming, therefore, a cast-iron piston ring in an aluminium piston may have a very detrimental effect upon the partially oxidized oil which is scraped from the cylinder walls into the ring grooves. At temperatures above 175° C. the metals, especially iron, increased the rate of oxygen absorption. When the metals were added in the form of filings or thin foil their catalytic effect was much more marked. Iron filings, for example, were found to increase the rate of oxygen absorption of several oils between 125° and 250° C. by as much as eightfold, and aluminium foil as much as threefold, when 0·1 g. of the metal was added to 1 g. of the oil.

Many attempts have been made to inhibit the oxidation of oils in the presence of air by the addition of small quantities, of the order of 1%, of 'stabilizers' such as cresol, β-naphthol, &c., which have shown beneficial results in preventing gum formation in volatile spirits containing unsaturated hydrocarbons. Their beneficial action in volatile spirits would naturally be at temperatures not above 20°–30° C. When tested with oils by the oxygen absorption method some of them were found to cause a reduction of the initial oxidation rate, but after an hour or so the effect became less and ultimately disappeared, probably as a result of the oxidation of the stabilizers themselves.

To set against the favourable showing of Pennsylvanian bright stock in Fig. 1. Thornycroft and Barton [1] have given the results of a series of 50-hour duration tests on a water-cooled engine which indicate that the addition of bright stock to a blend of mineral distillates increases the amount of carbon on the piston. Some of these results are given in Table I. The oils were prepared from refined distillates of the same origin, and the proportion of low and high viscosity distillates were adjusted so that the different blends with bright stock had approximately the same viscosity at 140° F. (60° C.). The results must be accepted with caution, not only because of the inherent difficulty of getting repeatability in such tests, but because, as the authors themselves point out, bright stock oils from different sources vary considerably in their carbon forming propensities.

TABLE I

Carbon formation with mineral oil distillates and blends with bright stock

	Blend of distillates	*Distillates 80 per cent. Bright stock 20 per cent.*	*Distillates 60 per cent. Bright stock 40 per cent.*
Oil consumption in 50 hours, pints	1·50	1·45	1·75
Carbon collected from the piston crown, gm. . .	0·43	0·90	1·43
Viscosity of unused oil by Redwood I at 140° F.	175·0	175·0	190·0
200° F.	58·0	60·0	66·0

The greater danger with the fatty oils of getting hard and gummy carbon deposits on the pistons in a hot engine (as distinct from a dirty appearance of the crankcase parts) is now generally accepted. It is only what might be expected from oils which are first cousins of the 'drying oils', and themselves absorb oxygen so readily at temperatures well below those prevailing in the piston. The figures in Table II, also taken from Thornycroft and Barton's paper, show that the addition of 5% of fatty oil to a mineral oil distillate caused an increase of rather more than 50% in the amount of carbon deposit during a 50-hour run.

TABLE II

The effect on carbon formation of fatty oil added to a mineral distillate

	Mineral oil distillate	*Mineral distillate +5 per cent. fatty oil*
Oil consumption in 50 hours, pints	1·55	1·45
Carbon collected from the piston crown, gm.	0·41	0·63

That a quite small addition of a really badly gumming oil should have a large effect upon the carbon deposits is only to be expected, when one considers how small a proportion of the oil consumed is actually concerned in forming the carbon deposits. During the 50-hour runs quoted in Tables I and II, for example, the amount of oil consumed was from 1·45 to 1·75 pt., or 650–800 g., while the total carbon deposits varied from 0·41 to 1·43 g. They varied, therefore, from 0·06 to 0·18% of the weight of the oil consumed. This constitutes a serious difficulty which affects the reliability of single-cylinder engine tests for classifying oils, for clearly quite a small change in the conditions of the test might bring about a large alteration in the weight of the deposits collected with any given oil, when so large a proportion passes out through the exhaust valve in a half-burnt condition.

There are chemical factors, too, unconnected with the type of oil as defined by its origin, which have been shown to affect the amount of sludge and carbon produced, to a degree quite as great as changes in the oils themselves. Thornycroft and Barton have given the results of two 50-hour tests using oils of the same viscosity, from the same asphaltic crude, in which a difference of the refining process led to carbon deposits at the end of one test nearly double those in the other.

Other tests at Ricardo's laboratory have shown that, during a 50-hour run in which the oil was circulated continuously and the sludge formed in the oil was collected in a centrifugal separator during the progress of the test, the amount of sludge was increased as much as fivefold when ½% of water was added to the oil after every 8 hours of running. Five different oils were tried, and the smallest increase in the sludge caused by the water was 33% in the 50 hours. Additions of water larger than ½% in 8 hours produced almost the same results, which were satisfactorily repeatable.

Although no water would normally be present in the lubricating system of an engine, there is undoubtedly the possibility of the condensation of water from the burnt gases during the starting-up period, and of this water reaching the oil in the crankcase. The quantity no doubt would be small, but might be sufficient to alter appreciably the sludging of the oil.

Oil Consumption

In any high-speed internal-combustion engine an amount of oil which is not less than 0·005 pt. per B.H.P. hour is consumed, and the amount may be ten times that figure in an engine which is due for overhaul. It may be taken that every bit of this consumed oil has by some means found its way up past the pistons into the combustion spaces; for the amount of direct leakage from the crankcase and valve gears can be reduced to a negligible proportion.

With the general trend towards high revolution speeds in engines for road vehicles this problem of oil consumption has become an important one; for at high speeds the combined effect of reduced piston-ring efficiency with wear of the cylinders and pistons may quickly produce an oil consumption which is altogether excessive. Even in aero-engines, where cylinder and piston wear is usually negligible, blockage of the drain holes in the pistons and scraper rings may cause a multifold increase in the rate of consumption.

Some of the oil left on the cylinder bores may perhaps be completely burnt to carbon dioxide and water, and pass out as such through the exhaust valve, but probably the larger portion is carried out by the exhaust gas in the form of semi-oxidized products and even, when the oil consumption is excessive, in the form of oil molecules and their cracked products.

The problem of reducing oil consumption is therefore purely one of limiting the amount of oil getting up past the pistons to what is necessary for cylinder lubrication; and it is of some interest to arrive at a sort of basic minimum figure, on the assumption, for example, that a film 1 molecule thick is removed by oxidation or evaporation every working stroke. Taking for the basis of one's arithmetic a 12-cylinder engine of bore and stroke $5 \times 5\frac{1}{2}$ in. and yielding 500 h.p. at 2,250 r.p.m., and assuming that the thickness of a monomolecular layer is between 10 and 20×10^{-8} cm., then the volume of oil consumed per hour would be from about $\frac{1}{10}$ to $\frac{1}{5}$ pt., or about $\frac{1}{25}$ of the minimum rate of consumption achieved in practice.

It has already been stated that even under the piston rings there must be a fluid film of appreciable, though widely varying, thickness, so that the film of oil left on the walls during a working stroke is probably on an average several thousands of molecules thick, and we may fairly conclude that when a 500 h.p. engine consumes only $2\frac{1}{2}$ pt. of oil per hour most of the oil consumed is actually burnt or evaporated off the cylinder surfaces, and that there is very little preventable waste.

If an engine can run safely at the minimum figure of 0·005 pt. per B.H.P. hour, then anything above that rate of consumption simply means that more oil than is necessary is passing the pistons, and the excess is being partially burnt or evaporated away; and the reasons why oil consumptions vary so widely and are sometimes ten times the minimum figure must now be considered.

The physical conditions which control the passage of oil up past a piston are still very uncertain. It used to be thought that the movement of oil to the combustion side of the piston was influenced by the gas pressure in the cylinder, and that the flow of the oil was more rapid when an engine was run throttled down because it was then aided by the partial vacuum above the piston during the suction stroke. This idea was proved to be fallacious by Ricardo, with a piston-testing machine in which the oil passing the piston was collected and measured while various gas pressures, ranging from a 20-in. vacuum to a positive pressure of 45 lb. per sq. in., were maintained above it. Changes of gas pressure were found to have no influence on the amount of oil collected.

The apparent increase of the amount of oil in the combustion space during throttled running is due to an accumulation of that normally passing, because the cycle temperatures are too low for the oil to be burnt and got rid of, as it is at full load. When the throttle is afterwards opened this accumulation of oil can only be very partially burnt, for lack of air, and the consequence is the well-known cloud of blue smoke.

The important factors in oil consumption, apart from piston design and the condition of tune of the engine, are the design and clearances of the connecting-rod big-end, which affect the quantity of oil thrown on to the cylinder walls; the viscosity of the oil at the piston temperature; and the speed. In a given engine, with a given oil, the rate of consumption depends almost entirely on the speed of revolution, and hardly at all upon the throttle position. In so far as the rate of oil consumption has been shown to increase with the load of an engine at constant speed, this is the result of a higher piston temperature which reduces the oil viscosity at the critical points, where it gets past the rings.

Some rational explanation of the process whereby the oil passes from the under to the upper side of a piston will now be attempted.

The practical man knows that within limits, at any rate, the use of a more viscous oil will mean a lower oil consumption; and that by the addition of 'scraper' rings to the piston, or by increasing the radial pressure and reducing the side clearance of existing rings, the same result can be achieved; but how and why the oil gets past the rings at all, at the rate that it does, cannot be explained by a reference to their 'pumping action' as they move up and down in their grooves when the piston motion reverses.

That the passage of the oil past the piston is closely bound up with the behaviour of the rings there is no doubt; but experiments to elucidate the part played by them have led to puzzling and inconsistent results, and it is clear that it cannot be dismissed by a simple reference to their pumping action. It must be remembered, in the first place, that apart from the slight rocking of the piston due to its clearance and the obliquity of the connecting-rod, the motion of the rings and piston is entirely symmetrical, end for end. There is therefore no obvious reason why the rings should pump oil one way more than another, except that fresh supplies of oil are constantly provided from below by the connecting-rod big-end. But this does not suffice to explain the one-way flow, for if one pictures a ring as shifting from top to bottom of its groove on account of the piston reversal, while the ring itself remains stationary at the ends of the stroke, any fluid pressure in the oil set up by the piston motion will have dropped to zero as it comes to rest, and there is then little reason why the oil should flow one way more than another just because the supply is more ample on the under side. A rather different sequence of events to explain the upward flow of oil, which does in fact take place, is outlined below.

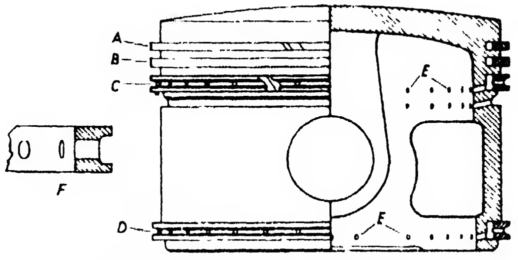


FIG. 2. Typical aero-engine piston.

The piston of a high-speed engine normally carries both 'gas' rings and 'scraper' rings. Fig. 2 shows an elevation and half-section of a typical aero-engine piston. It has 2 gas rings *A* and *B*, and 2 scraper rings *C* and *D*. It is the function of the gas rings to form a gas-tight joint between the piston and cylinder, and they are always disposed in plain, closely spaced grooves near the top of the piston. There may be one or two scraper rings, always below the gas rings, and if there is more than one, the second is often near the bottom of the piston skirt, as at *D*. The scraper-ring grooves are provided with drain holes, *E*, which connect the back of the groove with the under-side of the piston, and the rings themselves are commonly cut away as shown in the enlarged cross-section at *F* in the Figure. Such a form of ring enables a high pressure to be maintained on the cylinder wall and also provides a freer path for the oil scraped from the walls during the down stroke to reach the drain-holes. The open groove below the scraper ring *C*, also provided with drain holes, is to collect, and provide the first path of escape for, the excess oil from the cylinder walls.

The important part played by the scraper ring in the matter of oil consumption has been brought out by observations extending over long periods of running. It has been found, for example, that in aero-engines engaged upon a regular commercial service the rate of consumption increased from 5 to 25 pt. per hour between the beginning and the end of a period of 500 hours. After an overhaul, and removal of the sludge from the scraper-ring grooves and drain holes, the rate of consumption was reduced again to the lower figure.

Since the escape of surplus oil through the drain holes is clearly a vital factor, it is a fair conclusion to draw that when they become blocked a considerable fluid pressure is created below the ring during the down stroke of the piston, as the oil is scraped from the cylinder wall and trapped between it and the piston-skirt, with no free path of escape. When the piston does not carry a scraper ring at the bottom of the skirt, the fluid pressure will build-up on the lower side of the lowest ring. Normally this would be a scraper ring, and a large part of the trapped oil escapes through the drain holes to the under side of the piston. Omission of the scraper, or its ineffectiveness through inadequate radial pressure or through an inadequate size, or blockage of, the drain holes, is always accompanied by a high rate of oil consumption.

Some oil is of course left on the walls by the scraper and subsequent rings, and this can be understood as due to two circumstances. Firstly, no cylinder bore and no piston-ring surface is perfectly cylindrical, so that actual contact between the two must be only at points round the circumference, separated by lengths where there may well be a clearance of 0·001 cm. or less. And secondly, the scraping edge of a ring must be slightly rounded when considered on the scale of hundredths of a millimetre, and this, combined with the unevenness of the surface already referred to, may enable the ring to 'ride-up' on the oil film in the manner of the Michell bearing. Support for this conception is provided by the experience that at very high piston speeds, of the order of 3,000 ft. per min., something in the nature of a critical speed has often been observed at which the rings appear to lose control of the oil and the rate of consumption increases very rapidly [3]. At such a speed one may suppose that the average pressure under the working surface of the ring becomes equal to the radial pressure due to the elastic forces in the metal. The break-down speed can be raised by increasing the elastic pressure of the ring on the cylinder surface.

Further support for the view that the piston rings are normally separated from the cylinder wall by a film of widely varying thickness is afforded by the fact that by careful equalization all round of the radial pressure exerted by the rings it was found possible to reduce the normal oil consumption of an engine by amounts varying between 25 and 100%; and also by the observations of Mougey [4], confirmed by Ricardo, that, although at moderate speeds an increase of viscosity reduces the rate of oil consumption, there may come a point in high-speed engines beyond which this is no longer true. The phenomenon is only noticeable at high speeds. The rate of increase of the consumption with speed of a highly viscous oil becomes much more rapid beyond a certain point, and its consumption as compared with a less viscous one at lower speeds becomes reversed. These are results which can be explained on the supposition that the high viscosity, while reducing the oil-flow round the back of the rings, enables the rings to ride over, and leave behind, a thicker film on the cylinder wall.

The calculation given earlier showed that the minimum practical consumption of 2½ pt. per hour in a typical 500 h.p. engine corresponded to the removal of a film about 25 molecule diameters thick, or, say, $2{\cdot}5\times10^{-6}$ cm. The average film left by the rings due to unevenness of the surfaces may easily be many times thicker than that, so that there is no need to seek for a further explanation in regard to the oil which gets past the rings and is consumed in a well-designed cylinder with efficient scraper rings.

When, however, owing either to the design or to blockage by sludge, the fluid pressure built up below the rings is not adequately relieved, it seems likely that the excessive oil flow past the rings which then occurs is due to a different phenomenon. During the descent of the piston, until the point of maximum velocity is reached at about mid-stroke, the rings must be held against the upper surfaces of their grooves by their own inertia, by surface friction, and by the fluid pressure which is rapidly building up beneath them. Beyond the point of maximum velocity the rings will remain at the tops of their grooves only so long as the friction force, aided by the fluid pressure, is greater than the inertia force on the ring. In a high-speed engine the inertia forces are very large. In the typical engine for which the oil consumption was given earlier the mass of one ring is just under 2 oz. and the inertia force upon it due to the deceleration of the piston is, at the end of the stroke, no less than 50 lb. at a speed of 2,250 r.p.m. It is impossible to say what the fluid pressure in the oil may be, but one may deduce from the mechanical efficiency of the engine that the average friction force between one ring and the cylinder surface cannot be more than 10 lb. at the outside. Direct experiment has shown that, on a piston 5½ diam., when there are several rings present, the average friction force per ring is about 6 lb. It is clear, therefore, that long before the end of the down stroke, while the piston velocity is still high and while there is still a big fluid pressure below the rings, the inertia of the ring will cause it to leave its seat against the upper surface of its groove and to move down to the lower one. While the ring moves from the top to the bottom of its groove there is a free passage open for oil to pass round behind it from its lower to its upper side under the fluid pressure. As the speed of revolution is increased, not only is the average fluid pressure increased thereby, but also the rapidly increasing inertia force upon the ring will cause it to leave its seat earlier on the down stroke than before, when the piston velocity is nearer to its maximum.

This picture of what probably takes place attempts no more than a qualitative explanation, but so far as it goes it does appear to fit all the facts. It is consistent with the observed effects of oil viscosity and of the functioning of the scraper ring upon the rate of oil consumption, and it explains the very rapid increase of the consumption with an increase of revolution speed. This variation with speed is by no means regular, but has been found to be roughly proportional to between the square and the cube, with an increase even more rapid when the critical speed already referred to is approached.

The outline given above appears to offer an adequate explanation of how the oil gets from the lower to the upper side of a ring during the down stroke. The reverse process does not happen upon the following up stroke for several reasons. For one thing there is no ample supply of oil present to build up the fluid pressure above the rings. The only oil there is what was left behind after the previous stroke. Equally important are likely to be the facts that the main gas rings are near the top of the piston and that the piston clearance above the rings is normally greater than below them. Instead of having a long and narrow space for the fluid pressure to build up in one has, therefore, a very short and a wider one. This, and the scarcity of oil, are sufficient to explain why the balance of flow is upward past the rings.

Apart from the broad questions of the number and design of the scraper rings, there are many points in the detailed design of a piston, and its condition, which may profoundly affect the rate of oil consumption. An increase of the side clearance allowed between the rings and their grooves, for example, invariably puts up the rate of oil consumption: a fact which is clearly consistent with the suggested description of how and why the oil gets past the rings; as, also, are the observed effects of speed and of the viscosity of the oil at the working temperature.

In aero-engine pistons the side clearances of the rings are generally graduated from about 0·008 in. in the top groove to 0·003 in. below the second ring; for although the smallest clearance would give the lowest oil consumption it is found that a small clearance where the piston is very hot leads to rapid gumming of the oil in the grooves and to sticking of the rings. A clearance of at least 0·008 in. is necessary in the top groove to allow the first gummy products of the overheating of the oil to be washed away by fresh supplies.

In road-transport engines wear during service is of great importance, both ovalling of the cylinder and piston, and also in the form of an increase of the side clearance of the rings. Ottaway [5] has given figures relating the percentage increase in the rate of oil consumption between the beginning and end of a running period of 20,000 miles with the wear of the top ring groove per 1,000 miles. His results covered four different types of piston, for which the rates of wear were 0·00012, 0·00025, 0·00027, and 0·00040 in. per 1,000 miles. The corresponding increases in the rates of oil consumption during the period were 21, 41, 53, and 140 per cent. The two were thus roughly proportional, except for the piston showing the most rapid wear, with which the oil control had for some reason deteriorated more rapidly.

The importance of ring groove and other forms of piston wear was further demonstrated by running new pistons and rings in worn cylinders, and vice versa. In the former case the rates of oil consumption were comparable with those in new engines, whereas old pistons in new cylinders continued to show an excessive oil consumption.

For much further information about oil consumption in road-transport engines the reader is referred to the papers by Mougey and Ottaway already mentioned.

REFERENCES

1. Thornycroft, O., and Barton, C. H. *Aircraft Engineering*, Feb. and May 1930.
2. Barnard, D. P., and others. *J.S.A.E.*, **34** (5), 127 (1934).
3. Taylor, *J.S.A.E.*, 1931.
4. *J.S.A.E.*, **29** (3) (1931).
5. Ottaway. *Proc. Inst. Aut. Eng.*, 26, 150.

LUBRICATION PRACTICE

By Lt.-Col. S. J. M. AULD, O.B.E., M.C., D.Sc., M.Inst.P.T.
Chief Technologist, Vacuum Oil Company Ltd.

THIS article deals with the lubrication of industrial machinery of different types, and is mainly concerned with the following:

1. Diesel engines.
2. Steam engines.
3. Steam turbines.
4. Industrial gears.
5. Textile spindles.
6. Refrigeration machinery.

DIESEL ENGINES

The purpose of lubrication of these prime movers is firstly, of course, to reduce friction between rubbing surfaces. There is in addition, however, the important function of maintaining effective piston-ring seal so as to prevent leakage of the cylinder gases. In practice the lubrication of the (power) cylinders, including the sealing function, must be considered separately from lubrication of the external and subservient parts.

Cylinders

It is necessary that the oil film be produced and maintained or renewed effectively throughout the cycle despite its exposure to the high temperatures and pressures which are encountered at the combustion end of the cylinder for a considerable part of the power stroke. This may be done by positive lubrication or by oil splash or throw.

Force feed is generally used in large engines for lubricating the cylinder walls, the number of points to which oil is fed being dependent upon the bore and stroke. As a rule the distance between points in large engines should be of the order of 12 in., though this distance is sometimes greatly exceeded. The greater the distance, however, the more attention must be paid to the selection of the oil to ensure even distribution. Increasing the number of points does not necessarily increase the consumption, since much smaller quantities of oil can be fed to each point.

In 4-stroke vertical engines the oil is generally introduced between the first and second piston-rings when the piston is at the bottom of its stroke. In 2-stroke vertical engines the feeds are generally located above the ports in such positions that only the minimum amount of oil is lost through the ports. It is to be noted that with good oil and a satisfactory mechanical lubricator in use no choking is experienced from the inlets being exposed to the hot combustion gases. Two-stroke engines of large horse-power per cylinder are sometimes given small additional feeds about one-third of the stroke from the top to supplement the oil film on the parts of greatest wear.

Horizontal engines of large size generally have three feeds per cylinder spaced around the upper half between the position of the first and second piston-rings at outer dead centre of the crank. Small engines have one feed only.

When the bearings are lubricated through a circulatory system the cylinders may be lubricated by oil thrown up by the cranks. In this method of application the oil pressures must not be too high or there is danger of excessive lubricant being thrown on to the cylinder walls. There is also a tendency to create an undue amount of oil mist in the crank chamber where in the heated atmosphere oil in such condition is liable to oxidize.

In many high-speed engines both cylinders and bearings are lubricated by splash. Fig. 1 shows such an arrangement. The oil is contained in a sump in the crank chamber whence a pump delivers it through a filter to trays under the big-ends. The specially designed big-ends dip into the trays and splash the oil over all the working parts.

Bearings

Nowadays almost all compression-ignition engines are entirely enclosed, and this design has rendered possible the use of either full-force feed circulation or gravity feed for bearing lubrication.

Ring or collar oilers, &c., may be employed both for main or subsidiary bearings, the oil being contained in the lower part of the bearing housing. When such means are adopted it is essential to clean out the reservoirs at regular intervals and to replace with clean oil.

In all these systems, whether circulatory or semi-circulatory, as much lubricating oil should be carried as practicable. The larger the volume the longer will be the life of the oil and the more readily can it be cleaned or recovered.

Selection of Oils

It is apparent from the foregoing that cylinder and bearing lubrication ought to be considered separately; yet exigence frequently demands that a single oil be used throughout even when the cylinders are not splash lubricated. In such cases a compromise has to be effected, and it must be realized that ideal lubrication may not be obtained from either system. In these instances the power cylinders must be given primary consideration. Here the conditions are particularly severe at the end of the compression stroke and the beginning of the power stroke. Temperatures are at their highest; piston rings are being pressed against the cylinder walls; and the piston in its reciprocating motion slows down and actually comes to rest before commencing the return stroke. Under these conditions boundary lubrication undoubtedly occurs, at east momentarily.

Choice of oil in these circumstances may certainly be guided by specification, but is to a much greater extent a matter of experience. It is best founded upon knowledge of the oil, of the nature, size, and conditions of operation of the engine, and of the method of lubrication. This applies even to the relatively simple matter of choice of viscosity. Effective distribution is dependent on fluidity and the movement of the piston, and if the oil be too viscous it is carried along in streaks resulting in poor lubrication and incomplete piston-ring seal. On the other hand, an oil too light in body, though spreading rapidly over the surfaces, may be unable to maintain an efficient lubricating film. This will automatically result in liner and piston-ring wear and ultimately in piston seizure.

The same effect is liable to be produced with oils of inferior quality even if fed in liberal quantities. Oils for the power cylinders of Diesel engines must be capable of withstanding the high temperatures and pressures encountered. Without such stability they are likely to form gummy deposits which will interfere with the full movement of the piston-rings.

It is interesting to note how, with the vast improvement in the quality of mineral lubricating oils in recent years, there has developed a tendency to use oils of lower viscosity for cylinder lubrication. This is quite sound, as is also the continued departure from the use of compounded oils. In the past compounding was more frequently resorted to than nowadays for the purpose of increasing the oiliness of Diesel lubricants. There were serious disadvantages attached to this procedure, chiefly of gumming and carbon formation. Now that even highly refined mineral oils are so much better in respect of lubricity the significance of compounding for power-cylinder lubrication seems largely to have disappeared.

If a separate oil is used for the bearings it is generally less viscous than that for the cylinders, especially in big engines. This may not apply where application is made by all-loss systems owing to the greater difficulty of maintaining the oil wedge. With circulatory or semi-circulatory systems the oil should be readily separable from water and other adventitious impurities. It should also be highly resistant to oxidation and sludging, not only to ensure its longer efficient life in the engine, but to assist in its recovery—an important part of all large Diesel lubrication systems.

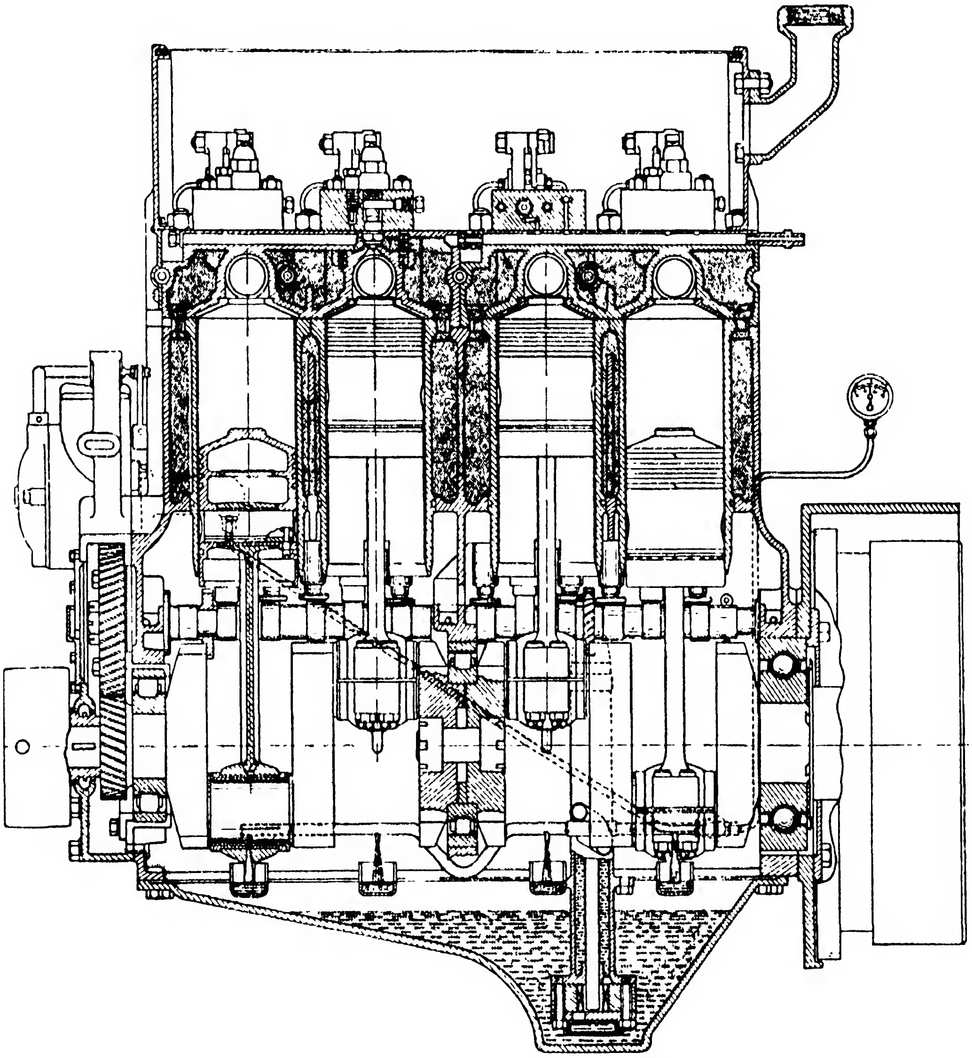


FIG. 1. High-speed compression-ignition oil engine arranged for splash lubrication. (*Courtesy Vacuum Oil Company, Ltd.*)

Where air-compressors are used it may be necessary, owing to moisture in the intake air, to use compounded oil for the compressor cylinders. This assists in the formation of a film which will not wash away. There is, however, a growing inclination on the part of engine users to use mineral oil whenever the air is not excessively moist. This necessitates special attention being paid to draining of the intercoolers. Whatever the oil used, however, it must be of the highest grade as regards stability and used in the smallest possible quantities.

Selection of lubricating oils for compression-ignition engines is frequently made the subject of the framing of specifications. The value of such specifications as broad classifications may be accepted. Their use is frequently accompanied, however, by some danger of misdirection and limitation of choice. In this connexion the following specifications recently issued (December 1934) by the Diesel Engine Users' Association are of interest:

Specification for Lubricating Oils for Use on Heavy Oil Engines

	L. 1	*M. 1*	*H. 1*
Sp. gr. at 60° F. (max.)	0·882	0·885	0·888
Closed flash-point (min.)	400° F.	400° F.	400° F.
Viscosity Redwood:			
at 70° F. (max.)	700 sec.	1,250 sec.	1,800 sec.
„ 200° F. (min.)	50 „	56 „	68 „
Pour-point (max.)	35° F.	35° F.	35° F.
Colour	clear red or yellow	clear red or yellow	clear red or yellow
Demulsibility	2 min.	3 min.	4 min.
Total sulphur (max.)	0·5%	0·5%	0·5%

	L. 2	*M. 2*	*H. 2*
Sp. gr. at 60° F. (max.)	0·915	0·918	0·920
Closed flash-point (min.)	375° F.	375° F.	375° F.
Viscosity Redwood:			
at 70° F. (max.)	1,300 sec.	. .	. .
„ 140° F.	. .	190 sec.	230 sec.
„ 200° F. (min.)	52 „	60 „	68 „
Pour-point (max.)	35° F.	35° F.	35° F.
Colour	clear red or yellow	clear red or yellow	clear red or yellow
Demulsibility	4 min.	6 min.	8 min.
Total sulphur (max.)	0·8%	0·8%	0·8%

The oil to be a STRAIGHT MINERAL OIL.
Method of Testing: I.P.T.

The two sets of figures are intended to represent different qualities of oils. It is stated that the M oils are of such viscosities as to meet all requirements from the highest to the lowest speeds. For engines running between 240 and 360 r.p.m. both M and L oils are expected to give satisfactory working; for engines operating below 240 r.p.m. the M oils are indicated. For engines operating over 1,000 r.p.m. either M or H oils can be chosen. No mention is made of horse-power, piston speed, or other conditions of operation. Though specific gravity, colour, demulsibility, and sulphur content are specified no attempt is made to measure chemical stability in any form.

As a general guide to the viscosities of oils suitable for particular conditions such specifications could be made useful. But as they stand they exclude some of the highest grade and best-known proprietary lubricants. The practice followed by most important engine builders of testing in their engines the products of such oil concerns as they think desirable, and only approving the use of particular brands and grades after long experience or searching test, has much to commend it. It ensures that the design, intended use, and even the idiosyncrasies of the engine are properly catered for. In the long run this method amply repays the trouble taken.

STEAM ENGINES

The internal and external parts of the steam engine are separately and differently lubricated. The former comprise cylinders and valves; the latter the bearings. Piston rods and valve spindles may be regarded as internal parts.

Cylinders, Steam Valves, &c.

Lubrication may be effected by direct application of oil to the individual parts concerned and with separate feeds to the cylinder valves and glands; or it may be done indirectly by atomizing oil into the steam line and using the steam itself to carry the lubricant to the moving parts. The latter is the usual and correct method. In certain cases, notably when large engines are under-loaded and atomization poor, it may be essential to take direct feeds to the valves. As a rule, however, direct lubrication is only adopted as an adjunct to atomization in difficult cases, and should be resorted to cautiously because of the difficulty of spreading heavy cylinder oils efficiently. Direct feeding is accomplished by means of a mechanical lubricator driven from a moving part of the engine.

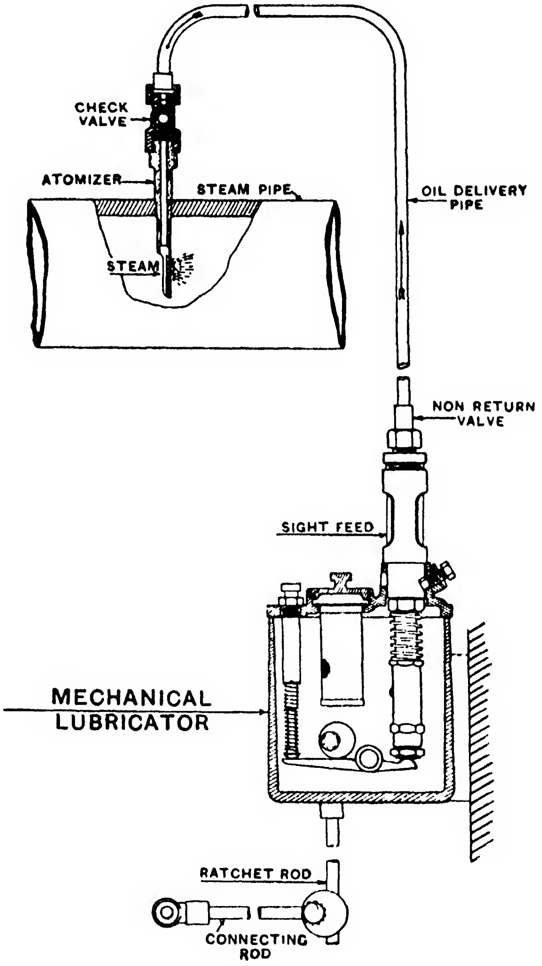


FIG. 2. Diagram showing a mechanical lubricator arranged to feed oil through a check valve and atomizer into a steam pipe. (*Courtesy Vacuum Oil Company Ltd.*)

The mechanical lubricator is also the best means of introducing oil into the steam line. Indeed, modern conditions of temperature and pressure have made its use almost a necessity. By its employment regulated quantities of oil are fed to the atomizer in the main steam line and thereby ensure economical operation by the use of the minimum quantity of oil. The converse is also true in that positive mechanical feed prevents all possibility of intermittent oil starvation as may happen with other methods. Fig. 2 shows diagrammatically the arrangement of a mechanical lubricator for feeding oil through a check valve and atomizer into a steam pipe.

The choice of oil for steam-cylinder lubrication is determined by the pressure, condition, and subsequent disposal of the steam; and by the size, speed, and load of the engine.

Steam Conditions. The higher the pressure the more viscous must be the oil in order to cope with the higher temperatures involved. Generally speaking, the reverse is also true, though special consideration must be given to the condition of the steam and the engine design, either of which may demand heavier oils even at low pressures.

High-grade cylinder oils are usually compounded with selected animal or vegetable oils. This is particularly necescessary with wet steam in order to give an adherent and tenacious emulsified film which will resist the scouring effect of the steam on the working surfaces. The practice of compounding is also applied with advantage to saturated and superheated steam where the extreme heat calls not only for oils of higher viscosity but also of higher lubricity. The fixed oil used for compounding is carefully chosen according to its purpose; and whereas for wet steam conditions and low loads and pressures rape oil or blown rape oil is largely used, it is desirable for the more severe conditions of superheat and high speed and load to choose an oil of as great chemical stability as possible.

Other oils are often used. It must be remembered that for superheat purposes, apart from choosing an oil of high heat-resisting qualities in order to prevent gumming and carbon formation, the oil must be readily atomizable. Superheated steam is not a good carrying medium for lubricating oil. Not only, therefore, must the oil itself split up readily, but it is best to introduce it into the steam line as close to the engine stop-valve as practicable.

Where exhaust steam is condensed on surface condensers and fed back to the boiler, it may be necessary to use a straight mineral oil in order to get ready separation from the exhaust steam by an oil extractor. The same consideration often applies where the exhaust steam is used in factories for process work. In many cases the process steam must be wholly free from oil, and this condition can only be attained by the use of an uncompounded product.

Engine Conditions. The viscosity of the oil chosen must bear some relationship to the size of the engine, or rather to the weight of the working parts. An example of this is the support of the pistons in certain horizontal engines. Speed is similarly effective, but in the opposite direction. Up to a point the higher the speed the less viscous need the oil be from the purely lubricating aspect. In addition to this it will be realized that for high speeds an oil is required which will atomize well and which will spread quickly over the working surfaces. This can only be obtained from a properly balanced oil of relatively low viscosity.

Engine load is also an important feature in governing the selection of the cylinder oil. At normal or high engine loading the steam velocities are high. As a rule this condition aids the atomization and distribution of the lubricant. There is no cause when operating under such conditions for departing from the reasoned choice of any oil because of its high viscosity. But at medium or low loads, or indeed at anything less than 75% of the engine's rated capacity, steam volumes may be so reduced as seriously to affect oil distribution. It may then be necessary to use an appreciably lighter oil to attain the degree of subdivision required for efficient lubrication.

With all these varying factors and requirements—many apparently operating in opposed directions—it may be difficult to come to a conclusion regarding the oil to be chosen. More probably with steam engines even than with other forms of machinery, the final decision is likely to be one based on experience.

Bearings

The external lubrication of the steam engine is carried out on generally conventional lines. The most important feature is the provision of an adequate and regular supply of oil.

If mechanical lubrication is adopted for the steam-line feed, then it is likely that this method will also be used for the bearings. It is strongly to be recommended. A mechanical lubricator with positive feed can ensure absolute precision in amount and application, and by this means permit the use of minimum quantities and lighter oils. These factors are of considerable importance in the efficient and economical lubrication of an engine.

Where it is possible or expedient to use a circulating system either pressure-force feed or gravity feed may be adopted. In the former a pump forces the oil from the main reservoir through the bearings concerned and possibly through a filter and cooler back to the reservoir. In the gravity system the oil is pumped to an overhead tank and passes thence generally through sight feeds to the bearings.

Whichever method is adopted it is essential that ample oil be in use, and that sufficient time be afforded for the many impurities collected on the way around the engine to settle out. Make-up oil should be added continuously or at regular intervals. It may also be possible to arrange for continuous treatment of the oil, in which case an aliquot part is withdrawn at frequent intervals. This is recovered by usual processes of steaming, settling, and filtration, and then returned to the system with the make-up oil.

Splash lubrication in steam engines is practised almost entirely on relatively small high-speed types. In these cases the engine is vertical and enclosed, the lower part of the chamber being utilized as an oil reservoir. The connecting-rod big end dips into the oil and splashes it to the other bearings. This method of lubrication is very effective, but intrusion of water is likely and special oils have to be used and special precautions taken to effect its separation. Owing to the continuous churning of the oil this is sometimes very difficult. In some cases, indeed, no attempt is made to separate the water. A highly compounded oil is used instead, and the engine lubricated with the creamy emulsion thus formed with the water which has leaked in or condensed.

Usually, however, a straight mineral oil is used with circulating or semicirculating types of lubrication. The latter include ring-oiler systems which are very efficient at low speeds and much used on crankshaft main bearings. Special attention must be paid in all these cases to the resistance of the oil to emulsification and to its ease of separation from adventitious impurities and sludge.

The viscosity of the bearing oil is determined other than by method of application by the size and type of bearings and by speed and load. Operating temperatures are generally taken care of in enclosed systems by altering the rate of circulation and thereby the transference of conducted and generated heat.

Size of bearing being presumably determined by the load to be carried, these points are affected simultaneously. The oil must definitely be capable of carrying the load and, apart from the accumulation of knowledge in this direction and widespread experience of particular grades and types of oil, many quite effective methods of calculation of the requisite viscosity have been evolved. They are naturally empirical, but have certain value in permitting decision as to the margin of safety to be allowed. It is to be remembered that the larger the bearing the greater the frictional surface and the need for good spreading qualities in the oil in addition to viscosity.

Speed, by carrying the oil forward and inducing the formation of the all-important oil wedge, is of great importance in bearing lubrication. The higher the speed up to certain limits, the less viscous need the oil be. At low speeds, on the other hand, it is most important to have sufficient body to the oil to ensure the formation of a sufficiently strong film.

Specifications for Steam-cylinder Oils

So many factors affect the choice of steam-cylinder oils that it is quite impossible to do more than give a broad guide to the selection of the types which should be used under average working conditions. Such a guide is given below in concise form.

Steam-cylinder Oils

	Wet steam	*Dry steam over 100 lb. pressure and superheated steam up to 600° F. at engine stop valve*	*Superheated steam over 600° F. at engine stop valve*
Specific gravity .	0·905	0·905	0·905
Flash-point, open .	500° F.	550° F.	575° F.
Redwood viscosity			
at 100° F. . .	1,400 sec.	1,900 sec.	3,100 sec.
„ 140° F. . .	410 „	580 „	855 „
„ 212° F. . .	94 „	132 „	171 „
Compound ingredient	6%	6%	6%

STEAM TURBINES

The lubrication of the bearings of steam turbines is carried out by force-feed circulation. After being pumped through the bearings the oil is returned through piping to a settling tank, thence through a filter to a tubular cooler, and then via a header once more to the individual bearings. The quantity of oil passing to the separate bearings is governed by regulating valves. When an oil-relay governor is used the same oil as for the bearings is generally employed and indeed is often supplied by the same pump. In the latter case a by-pass and relief-valve drop the pressure to the level required for the lubrication system.

The oil in a steam-turbine circulating system is subjected to very severe conditions. It undergoes continuous alternation in temperature from the bearings to the cooler; it becomes contaminated with water to a greater or less extent; and in its rapid circulation it is exposed to oxidizing conditions which are liable to deteriorate all but the most stable oils.

The most troublesome features in the behaviour of the oil are the formation of sludges or solid deposits and the formation of emulsions with intruded water. Both are ascribable to the oxidizing action of the air under conditions of heat and moisture.

The choice of a turbine oil is therefore fraught with much importance. If it is insufficiently refined varnish-like deposits may result. If it is over-refined the acidic oxidation products may result in the formation of metallic salts and oxides which, by adsorption at the interface between oil and water (especially in the presence of soluble oxidation products), may form such stable emulsions that the whole system becomes poisoned.

It follows that a turbine oil must be such as to maintain a balance between its lubricating value, its ability to separate from water, and its type of oxidation. In this respect knowledge of a turbine oil can only be acquired, as in other cases of lubrication, by observation of its behaviour under practical conditions. Nevertheless a preliminary classification, such as that of the British Standards Institution, is of extreme value in excluding oils which would be unsuitable. The B.S.I. Specification 489 is given below.

Care of Turbine Oil.

The greatest care and attention should be paid to the oil in circulation if trouble and eventual replacement are to be avoided. Samples should be taken at regular intervals—say once a month—and determinations made of the separating properties and extent and nature of the oxidation.

Much can be done for the oil by way of design of the circulatory system. There should be ample capacity so as to give the oil time to rest and permit separation of its impurities in the settling tank. The latter must be fitted with an efficient drain-cock at its lowest point and, if possible, should be baffled so that the pump suction can be taken from settled oil.

In the piping system foaming with its attendant aggravation of oxidation can be minimized by avoiding all sharp bends and abrupt changes of direction and by streamlining the omnibus return pipe. Suitable means should also be adopted for preventing splashing of the oil on its return to the tank. Whether to regard the intrusion of water by gland leakage as an entirely objectionable feature is a moot

	Viscosity (Redwood No. 1), seconds													
	At 21° C. (70° F.)		*At 60° C. (140° F.)*		*At 93·3° C. (200° F.)*		*Flash-point (closed) not less than*	*Cold test (oil to remain liquid at all temperatures above)*	*Sludge at 150° C. (302° F.) not exceeding*	*Volatility (loss by evaporation on heating) not exceeding*	*Total acidity mg. KOH per 100 g. of oil not exceeding*	*Demulsification test not exceeding*	*Total sulphur not exceeding*	*Deleterious sulphur*
Grade	*Max.*	*Min.*	*Max.*	*Min.*	*Max.*	*Min.*								
									%	%		*minutes*	%	
Light .	450	..	75	60	..	40	180° C. (356° F.)	0° C. (32° F.)	1·5	0·5	10	2	0·3	nil
Medium	680	..	90	75	..	42	180° C. (356° F.)	0° C. (32° F.)	1·5	0·5	10	2	0·3	nil
Heavy .	850	..	112	90	..	45	180° C. (356° F.)	+2° C. (35·6° F.)	1·5	0·5	10	4	0·3	nil
Extra heavy .	1,300	..	140	112	..	51	180° C. (356° F.)	+2° C. (35·6° F.)	1·5	0·5	10	6	0·3	nil

point. It is true that in a 'dry' turbine trouble from emulsions is absent. But the water in a 'wet' system may assist in the removal of water-soluble oxidation products and in that way help to maintain a clean system.

The circulating oil should be cleaned regularly by filtering or centrifuging. Centrifuging is best. It is now common practice in the larger installations to install a centrifuge integral to the system whereby a constant portion of the oil is withdrawn, cleaned, and returned. The proportion removed and the period necessary to operate the centrifuge are, of course, determined by the general condition of the oil. It is to be remembered that the best temperature for settling is not necessarily the best temperature for centrifuging and that, whereas a higher temperature in the main tank may facilitate the separation of gross impurities and water, it may be desirable to centrifuge at as near atmospheric temperature as possible. There may be, and in fact often are, impurities—chiefly oxidation products—which are soluble at elevated or operating temperatures but which precipitate on cooling. It is for the removal of such materials that treatment at atmospheric temperatures is desirable.

The periodical testing of the oil should be directed towards noticing

(*a*) formation of deposits or sludges;
(*b*) increase in specific gravity, viscosity, and neutralization value;
(*c*) reduction in ability to separate from water.

It is definitely not possible to give limits for these figures. The nature of a deposit may be far more important than its extent. Formation of gummy or resinous deposits must be looked upon seriously and steps taken to renew or recondition the oil. This also applies to loss in separating power, which may be caused by similar types of material.

The importance of the *nature* of the products measured by neutralization value (N.V.) has already been touched upon. In the case of the oil-soluble petroleum 'acids' of high molecular weight the formation of which characterizes certain oils the N.V. may, without causing any alarm, be many times that which would have to be regarded as a danger-line in others. What may be of importance in each case is the rate of increase. This also applies to the viscosity. Any unexplained acceleration of change must be explored. It is for such purposes that the maintenance of accurate test logs for each turbine is of importance.

Choice of Steam-turbine Oil.

For direct connected turbines the oil may be as light as possible compatible with its ability to lubricate the bearings satisfactorily under all conditions. The most severe conditions are, of course, those of starting and stopping. The grades usually employed are the 'light' and 'medium' of the B.S.I. classification. With increasing loads and severity of operating conditions there is nowadays a tendency to use the 'medium' to a greater extent than formerly.

Where connexion to the driven unit is through gears and the same oil has to be used for both bearings and gears, the 'heavy' oil of the B.S.I. classification is generally employed. This may be merely a compromise since the gears (see the section on Gear Lubrication) may call for a relatively viscous oil to withstand the loads transmitted. In such cases it may be necessary to have separate circulating systems for gears and bearings. The former may possibly then be lubricated with an oil of say 260 sec. Redwood viscosity at 140° F., whilst a B.S.I. 'light' oil of 65 sec. at the same temperature is used in the main bearing circulatory system.

Once the grade or grades have been decided upon actual choice of the oil should be based upon knowledge of its stability under practical conditions. None but the highest grade materials should be used. Needless to say, the oils must be uncompounded, though search has been made for suitable inhibitors or antioxidants with the idea of assisting the resistance of the oil to oxidation.

INDUSTRIAL GEARS

Correct lubrication is possibly the most vital factor in the efficient operation of a gear. Reduction of power losses and wear, and incidentally of noise, are direct results of the proper choice of lubricant, and are quickly reflected in reduction of operating and maintenance costs.

Gears are called upon to transmit power under all sorts of conditions of speed and load, but consideration of the principles of operation will indicate the reasons for choice of particular types of oil or grease for individual conditions. Gears fall into two main classes—spur and bevel gears, and worm and spiral gears. Each type has its own problems, but it is to be remembered that in both classes, in addition to lubrication, the lubricant must act as a cooling agent. Method of application and quantity in use must consequently be given close consideration in addition to the physical and physico-chemical properties of the oil.

Gear lubrication is different from most other machinery lubrication in that in place of the rubbing surfaces being flat to flat, or convex or concave to convex, gear teeth are convex to convex. The effective area of contact is consequently very small, and the pressures per unit area are proportionately magnified. Moreover, in spur gears the existence of the oil wedge is short, and though prolonged in the case of worm gears this advantage is discounted by other conditions. Generally speaking, then, gear lubrication must be classed amongst the most severe and difficult of lubricating operations. Even at comparatively low temperatures the intense pressures involved frequently predicate the existence of boundary lubricating conditions. The oil then becomes only secondary to design and manufacture in controlling the power transmission.

It will be apparent from the foregoing that the selection of gear lubricants must be influenced by the nature of contact of the gear teeth, by the loads and speeds, and by the operating temperatures. These conditions may vary from case to case. There is also the question of method of application. In addition lubrication may be involved in considerations of imperfection of construction or alinement, both of which are frequently adverse factors in gear operation.

Spur and Bevel Gears

In theory the contact between the teeth in these cases is along a line; but under load this becomes a band of greater or less width according to the correctness of design of the teeth and the nature of the metal. The movement is a combination of sliding and rolling. The former is at a maximum when the teeth first engage, but decreases to zero as rolling motion wholly supervenes at the moment of passing the pitch line. Thereafter sliding increases to a maximum again. Sliding motion can be very hurtful to poorly lubricated gears, but it assists in the formation of an oil wedge and is consequently of great assistance to lubrication when a suitable product is in use. Rolling motion may be very severe in its effect, and is particularly so at the moment of its maximum. With increase of load the pressure may then test the oil film to its utmost. It is important to remember, therefore, that load is directly proportional to the power transmitted and inversely proportional to the diameter and speed of the gear. It is on these factors that choice of viscosity and oiliness of the lubricant are based. With light to moderate loads, especially at high speeds, advantage may be taken of the stability and cleanliness of straight mineral oils. But with heavy and 'very heavy' loads, particularly at low speeds, a suitably compounded oil should be used.

Speed is of particular importance because of the time factor involved. At low speeds with high-power transmission there is time for the oil to be squeezed out from the pressure zone and the film ruptured.

It will be apparent that imperfections in the surfaces of gear teeth or faulty design will greatly magnify the normal effects of load and speed. Until corrected by running in, high spots may result in extreme localization of load with development of correspondingly intense pressures at the points of contact. Slight faults are likely to be eliminated by usage without appreciable damage being done to the gears; but serious imperfections may be quite incurable by running in or by choice of lubricant, and may result either in serious damage to the teeth or need for carrying lighter loads than is desired.

Closely allied to the pitting of gears due to definite imperfections is the flaking and pitting frequently noticed in new gears, sometimes to an alarming extent. This effect is usually on or adjacent to the pitch line. It is probably due to eventual formation of fatigue cracks caused by continuous subsurface stresses set up from gradual correction of teeth engagement rather than to individual faults. Both these types of surface wear may be treated with hopes of success by the use of specially chosen lubricants. Sometimes it is sufficient to produce a stronger film merely by use of a more viscous oil. In other cases it may be necessary in addition to employ a compounded lubricant containing fatty oil. This, indeed, is the most usual method. In bad cases, more particularly in gears operating at high speeds, the temporary use of extreme pressure lubricants may be called for. These products, of the sulphurized, chlorinated, or leaded type, are capable of maintaining lubricating films under intense pressures, and have frequently proved most effective in preventing wear during periods of correction.

Worm Gears

As in the case of spur and bevel gears, the contact between worm and wheel is along a line which in practice becomes a band of definite width. The relative rolling motion which goes on at the same time as the sliding of the surfaces over each other continually changes the position of this band and prevents concentrated wear on any one part. The sliding motion is claimed to increase the heat generated on the oil due to fluid friction, and hence to produce difficult conditions of temperature and pressure. It is certainly necessary in worm gears to use an oil of higher viscosity and greater lubricity than would be required for spur gears transmitting the same power. Increase of load, which is directly proportional to the power and inversely proportional to the peripheral speed of the wheel, magnifies this effect and is likely to produce a constant state of boundary lubrication in worm gears.

As in the case of spur gears, the lower the speed the heavier the body of the oil required. High speeds assist to carry the lubricant forward and maintain an oil wedge so that oils of relatively lower viscosity can be used and the fluid friction thereby reduced.

Methods of Application

The method of lubrication of gear sets varies according to the design, which in this respect varies from enclosure in oil-tight housings to complete openness. For the former force- or gravity-feed and splash oiling are generally used. For open gears it is customary to oil by hand or to use grease. Intermediate between these, semi-enclosed gears are often fitted with a trough containing lubricant through which the lower member passes.

In force-feed or gravity-feed circulating systems the oil must be capable of resisting oxidation even under the severe but usual conditions of being sprayed by nozzles direct into the gear teeth as they enmesh. Spray is always formed to a greater or less extent under such conditions, and aeration in this form at temperatures anywhere above normal will sludge any but the best oils. Temperatures can be kept low by the use of coolers and by keeping a large quantity of oil in circulation. These measures are particularly necessary if the oil is also to be used as a coolant, in which case it is fed to the outgoing side of the gears.

Oil for circulating systems must separate readily from water with which it may become contaminated. Other impurities, especially abraded metal and other adventitious solids, are removed by filters. It is essential that the oil be kept clean if it is to have a long life and do its work efficiently.

Most of the foregoing remarks apply equally to splash-oiling systems in which lower members of the unit dip into an oil-bath and carry or splash it to the remainder. With spur gears set in a vertical plane a more viscous oil than otherwise necessary may be needed to ensure retention on the teeth until the moment of engagement. In general, the positioning and rotation of the gears must be taken into account for the same reason.

For both spur and worm gears splash lubrication, by virtue of the limited opportunity of heat transference, demands more viscous oils than force-feed lubrication on gears of the same rating.

Hand oiling of open gears calls for no special description, but grease lubrication, especially of heavy-duty gears, may be of considerable importance. In steel-mill practice, and even on less onerous work where shock loads are encountered, grease and special products of heavy body capable of giving a cushioning effect are much used. Their composition is variable and is likely to be determined by the specific conditions of operation. For high-temperature work they may actually be solids which need to be applied hot. Whatever the consistency the gears must be carefully cleaned before the first application and the grease be of such a nature as to maintain a continuous and adhesive film.

Operating Temperatures

Temperature control is of much significance in the operation of gear sets. The following summary indicates the likely causes of temperature rise:

(1) Metallic friction due to imperfect tooth surface, misalinement, or insufficient strength of the lubricating film.

(2) Excessive churning of the oil in splash-lubricated gears, resulting from too high a level in the gear case.

(3) Excessive friction due to the formation of gummy or

other deposits following the use of an oil of unsuitable character and quality.

(4) Ineffective dissipation of heat, owing to the lack of sufficient radiating or cooling surface, or the use of insufficient oil in circulatory systems.

(5) External conditions such as hot surroundings, poor ventilation, or insufficient cooling water in units employing oil coolers.

Choice of Gear Lubricants

As indicated above, it is not generally practicable accurately to prescribe grades of lubricants for gears without knowledge of the individual duties and conditions of operation. The following tabulation gives a classification of gear oils which may be of some value:

Oil			*Spur, helical, and bevel gears. Totally enclosed. Pitch-line speed. Feet per min.*			*Worm gears. Totally enclosed. Rubbing speed. Feet per min.*	
Viscosity Redwood at 70° F.	*Viscosity Redwood at 140° F.*	*Compound*	*Cast iron or bronze*	*Steel up to 80 tons per sq. in. tensile strength*	*Steel case-hardened and over 80 tons per sq. in. tensile strength*	*Traction*	*Industrial*
..	..	..	1,000–2,500	5,000–	..	..	5,000–
1,200 sec.	130 sec.	..	500–1,000	2,500–5,000	5,000–	..	3,000–5,000
1,500 „	175 „	..	200–500	1,000–2,500	2,500–5,000	..	2,000–3,000
2,500 „	260 „	..	100–200	500–1,000	1,000–2,500	..	1,000–2,000
4,000 „	400 „	..	-100	200-500	500–1,000	..	–1,000 medium duty
..	525 „	5%	..	–200	–500	..	–500 heavy duty
..	750 „	7%	..	..	..	all	..

TEXTILE SPINDLES

The lubrication of textile spindles accounts for a large proportion of the light lubricating oil in use. In a large cotton mill the spinning department alone may contain as many as half a million lubricated spindle bearings. The general characteristics of the lubricating oils used are well known, but cleanliness and low power consumption are very important requisites.

Ring-spinning frames and ring-doubling frames constitute the most important and the bulk of the spindles in the textile industries. The spindles, which rotate at speeds as high as 11,000 r.p.m., revolve in oil-baths carrying inner tubes in which the spindles run. Since the clearances between these tubes and the spindles are very fine, the circulation of the oil between them is rapid, and it is essential that the oil be of low viscosity and high chemical stability. Actual lubrication is effected by the oil being drawn up on the spindle when in motion and returning to the bath by direction of holes or slots in the tube.

The lower the viscosity of the oil compatible with good lubricating qualities, and entire absence of tendency to thicken or gum, the greater is the power saving possible. The potentiality in the latter direction is marked, since over 50% of the power called for on the frame may be required by the spindles.

The oil is replenished as required either by lifting out the spindle or by use of a detachable oil cup.

The operation of the spindles on a ring-doubling frame for cotton is similar to that on ring-spinning frames for cotton or worsted, but the spindles are heavier and may require a rather more viscous oil. The same remarks apply to the spindles of ring-twisting frames for silk and rayon. In ring doubling by the wet method it may be necessary to grease the traveller rings and much work has been done in the development of suitable greases for this purpose.

Once the viscosity has been decided upon, the requirements of good spindle oil are summed up in a high degree of refinement and entire absence of tendency towards thickening or gumming under the conditions of use. The following physical characteristics are typical of spindle oils suitable under most conditions for the purposes named:

	Ring-spinning frames for cotton or worsted and rabbeth spindles	*Ring-doubling frames and silk and rayon twisting frames*
Specific gravity .	0·865	0·885
Flash-point, open .	320° F.	330° F.
Pour-point . .	15° F.	15° F.
Redwood viscosity:		
at 70° F. . .	75 sec.	175 sec.
„ 100° F. . .	52 „	83 „
„ 140° F. . .	40 „	50 „

Investigations carried out in conjunction with the 'Shirley Institute' research centre of the British Cotton Industry Research Association led to the development of a series of aerated lubricants based upon pure tallow and having the following specifications:

Extra soft	Melting-point	43° C.
Soft	„	45° C.
Medium	„	46·5° C.

The melting-points have a maximum tolerance of plus or minus 1° C.

Such greases will not solidify on the under side of the traveller rings, with the result that trouble from broken ends on starting up the frame from cold is largely eliminated. The 'Extra Soft' grade is used in the doubling of very fine counts at low room temperatures. It is also suitable for the rings on silk and rayon twisting-frames. The 'Soft' grade is applied for medium counts or for fine counts under warmer conditions; and the 'Medium' is used for coarser counts under normal conditions.

REFRIGERATION MACHINERY

There are three standard methods of mechanical refrigeration: (1) the so-called air system, in which compressed air, as an uncondensable gas, loses heat on expansion; (2) the compression system, in which a suitable gas or vapour liquefied by compression loses heat on evaporation; and (3) the absorption system, in which a gas, generally ammonia, is absorbed from cooling coils by water or an aqueous solution, the strong solution thus formed being evaporated and passed through a condenser to the coils again.

The absorption system involves no serious lubrication problems. The air system is cumbersome and little used nowadays. The compression system is by far the most commonly employed and demands special attention to the lubrication of the moving parts. This is the only method which is dealt with in the present article.

The Compression System

Briefly this consists of the repeated compression, condensation, expansion, and evaporation of a suitable refrigerant, which is either a low-boiling liquid or a liquefiable gas. The limits of cooling are set by the physical characteristics of the refrigerant and by the available temperature of the medium (generally water or air) used for carrying away the heat of compression.

In large- and medium-sized plants the refrigerants are usually ammonia or carbon dioxide. For smaller and domestic units a variety of materials are available. The most important are sulphur dioxide, methyl chloride, and dichlorodifluoromethane.

In all types of refrigerating machinery the problems of lubrication are closely bound up with the nature of the refrigerants, not only because of the different temperatures concerned, but because of their various chemical and physical action. The lubricated parts to be considered are chiefly the integral parts of the compressor—the pistons, valves, and stuffing-box; and the regulator or expansion valve which controls the flow of refrigerant from the high-pressure side to the low-pressure side.

Large-scale Units

It is common practice in modern refrigerating plants to use a central oiling system. This consists of a storage tank, oil filter, and water separator; and either a pump and sight-feed indicators or a mechanical lubricator. In this way the oil is used over and over again.

For the cylinders it is particularly important to judge the oil delivery carefully. If too little is used, friction and wear may take place and there may be leakage of the refrigerant past the piston. If too much oil is used, it will be carried over with the refrigerant and interfere with efficient heat transference by depositing on the inside of the condenser and evaporator coils. Even if otherwise thoroughly suitable, oil in excess may impede the operation of the expansion valve.

Stuffing-boxes are oil sealed, generally by pressure lubrication to a perforated bush situated between the packing rings. Excess oil returns to the crankcase.

Bearing lubrication is similar for refrigeration plant to that of other machinery and calls for no special description here. A separate oil may have to be used for the bearings of large machines.

The question of separation and recovery are very special features, however, and must be considered closely in connexion with choice of oils for internal lubrication. The oil separator, especially, is important, since its efficient operation prevents or limits the quantity of oil carried into the refrigerating system proper. Generally, if of a simple plate or helical-baffle type, it is situated in the compressor discharge line in advance of the condenser. The oil, it will be seen, must be of such a nature as readily to separate from the entraining gas and yet of such viscosity and condition that any carried forward is swept on by the refrigerant to a suitable drainage point and not deposited on the walls of the working coils or on the expansion valve.

Oil used in refrigerating machines must be absolutely anhydrous. Even traces of moisture can affect the operation of the plant by freezing to particles of ice which may clog the regulator valve. This is equally true of recovered lubricant. Such oil as is removed by drainage must be completely dehydrated by heat and carefully filtered before being returned to the system.

The general characteristics of a refrigerator oil may be summed up as follows:

(1) It must have ample lubricating qualities to prevent wear.

(2) It must be a straight mineral oil. Admixture with fixed oils is bound to result in gumming, in the formation of deposits, and in emulsification.

(3) The pour-point must be sufficiently low to allow the oil to remain fluid at the evaporation temperature of the refrigerant. This also ensures complete absence of wax, or other material, which might be deposited in the system.

(4) The oil must be highly resistant to heat and oxidation. Compression temperatures are high and a certain amount of air is liable to gain access to the system. Despite frequent drainage and filtration the system is liable to contain small quantities of abraded metallic oxides, of which copper oxide is particularly active as a catalyst. Condenser coils of carbon dioxide machines are frequently of solid drawn copper. Under these conditions it is all too easy to produce gummy oxidation or polymerization products from the oil.

(5) It must be chemically inert towards the refrigerant in use and not adversely physically affected thereby.

For ammonia and carbon dioxide machines an oil should be chosen meeting the above requirements and of the following approximate physical characteristics:

Pour test		−20° F.
Flash-point, open		370° F.
Redwood viscosity at	70° F.	575 sec.
,, ,,	100° F.	205 sec.
,, ,,	140° F.	80 sec.
,, ,,	200° F.	42 sec.

Automatic Refrigerators

Relatively small units such as are used in hotels and stores and also for domestic purposes are generally automatically operated by means of thermostats and refrigerant circulatory controls. They are fully enclosed. Internal lubrication is effected by an oil which in some cases is deliberately circulated with the refrigerant and in all cases comes into intimate and almost continuous contact with it. The behaviour of the lubricant under such conditions must consequently be taken carefully into account.

Methyl Chloride. When this refrigerant (b.p. −24° C.) was first introduced it was considered necessary to use a lubricant insoluble in it, and for a while glycerine was frequently employed. It was quickly found, however, that owing to the ready absorption of moisture by the glycerine it could not be used unless carefully protected from the atmosphere.

It is now fully realized that properly chosen mineral oils, although soluble in methyl chloride in all proportions, are the most suitable lubricants for this type of machine. At the compressor temperature and pressure the methyl chloride in the compressor does not sufficiently dilute the oil materially to reduce its lubricating efficiency. Moreover, experience has shown that under the conditions of operation the viscosity of the mixture of mineral oil and methyl chloride is not sufficiently lowered to imperil in any way the usefulness of a properly constituted oil.

It is also to be noted that solutions of oil and methyl chloride, of the concentration produced in a properly designed refrigerator, boil at only very slightly higher temperatures than pure methyl chloride, and therefore have only inappreciable effect on the temperatures reached in the refrigerating machine.

A suitable oil for methyl-chloride machines has identical properties to those given above for ammonia and carbon dioxide machines.

Ethyl Chloride. This material is used in certain low-pressure refrigerators, the boiling-point of the pure refrigerant being +12·5° C. Lubrication is not so straightforward as in the case of methyl chloride owing to the system being liable to periodic flooding with actual liquid.

As mineral lubricating oil is soluble in all proportions in ethyl chloride, it is usual to employ as lubricant glycerine or a mixture of glycerine and ethylene glycol. If a mineral lubricating oil is used, it must be of sufficiently high viscosity to retain appreciable body even when widely diluted with the liquid refrigerant.

Dichlorodifluoromethane. This liquid is used extensively in domestic refrigerators under various trade names and possesses properties claimed to be almost ideal. Its boiling-point is −30° C.; it is non-toxic, non-inflammable, and non-corrosive. As, however, its boiling-point is nearly the same as that of methyl chloride, it is equally liable to cause vapour or liquid dilution of the lubricating oil. For some reason the mineral oil generally employed for use with this solvent has usually been of higher viscosity than that used in conjunction with methyl chloride, but this is not strictly necessary.

A typical suitable specification is as follows:

Pour-point	−20° F.
Flash-point (open)	385° F.
Redwood viscosity at 70° F.	850 sec.
„ „ 100° F.	285 „
„ „ 140° F.	100 „

Sulphur Dioxide. In modern sulphur dioxide machines the refrigerant may be in very intimate contact with the lubricant and, in some cases, the machine depends for its efficiency on the deliberate carrying over of oil with the gas and subsequent separation of the oil from the liquid SO_2. It is essential, therefore, for the lubricant to possess very special properties.

In the first place, liquid sulphur dioxide is capable of dissolving certain fractions of mineral oils, and these fractions are frequently of a different nature from the bulk of the oil. It is necessary, therefore, that the lubricating oil should either have been previously so treated with SO_2 as to have the bulk of its sulphur dioxide soluble constituents removed, or else be of such a nature that the fraction dissolved and subsequently left behind when the liquid SO_2 vaporizes is not waxy or sticky, or in fact of different properties in any way from the ideal lubricant.

In the second place, there must be no chemical action between the sulphur dioxide and the oil, or between sulphur trioxide and the oil. Sulphur trioxide may be present in impure liquid sulphur dioxide, or it may be formed in small quantities by oxidation during operation, especially if the oil be in contact with iron oxide. Even the minutest traces of moisture will produce from SO_2 and SO_3 sulphurous and sulphuric acids respectively. Not only are these acids intensely corrosive towards all metallic parts with which they may come in contact, but the sulphuric acid, particularly, is capable of charring any oil which has been insufficiently refined, with the formation of carbonaceous material. Should such action take place, there is likely to be trouble. With these small machines the clearances are very small, and even the slightest deposition of gummy or carbonaceous material is enough to cause sluggishness in operation, and sometimes actual seizure.

For these reasons the ideal lubricant for sulphur dioxide machines should not darken appreciably even after continued contact with sulphur dioxide, and it should preferably not darken even when allowed to stand in contact with concentrated sulphuric acid. The oil must therefore be highly refined. Other characteristics should be approximately as follows:

Pour-point	−35° F.
Flash-point (open)	350° F.
Redwood viscosity at 70° F.	290 sec.
„ „ 100° F.	125 „
„ „ 140° F.	62 „

METAL WORKING OILS

By P. BEUERLEIN, V.D.I., *Hamburg*

In the fabrication of steel and iron metal cutting oils are extensively used. They may be divided as follows:

1. Oils for metal working in which cuttings are removed. Included in this class are the true cutting oils, used in boring, milling, turning, and other cutting operations. The oil serves the purpose of lengthening the life of the tool, reducing the friction between tool and work, improving the surface finish, and, in many cases, of conducting away the heat developed in the cutting operation.
2. Oils for metal working in which no cutting is involved. Such oils include those used in wire-drawing, pressing, and cold rolling. They serve to reduce the friction between tool and material and to improve the finish of the surface.
3. Tempering oils and similar products, used for quenching, tempering, and annealing operations, in which a liquid bath is necessary.
4. Anti-corrosion oils, used to protect the finished work from surface corrosion.
5. Oils used for 'burning' on to the finished work, to give a black, rust-resisting finish.

Class 1. Metal Cutting Oils

In cutting oils of the first class, differentiation is made between straight cutting oils, which are used as delivered from the manufacturer, and the so-called water-soluble oils, which are mixed with water before use, to form a white emulsion. Formerly vegetable and animal oils were mostly used as cutting oils. This is no longer the case, as these oils, on account of their unsaturated compounds (high iodine number), tend to resinify and in consequence may interfere with the feed and the mechanism of the automatic machines. At present very good results as regards cuttings and long life of the tools are being obtained with mineral cutting oils, without their having the above-mentioned disadvantages. Mineral cutting oils frequently contain sulphur in order to improve lubrication at the point where cutting occurs. Very high sulphur content causes the oils to become black and opaque. As this property is undesirable for certain purposes, there are limitations to the use of such high sulphur-content oils. No oils containing sulphur should be used for working bronze and similar copper alloys, or the work will become discoloured. In such cases pure mineral oils are used, which, in addition, are more stable towards the marked catalytic activity of these metals.

The viscosity of these cutting oils should not be less than 1·8° E. at 50° C., and the flash-point not less than 140° C. These analytical data, however, give little information on the behaviour of the oil during service, and reliance must be placed on the results of practical testing for this. The testing of the oil is carried out in the following manner: Under similar conditions of cutting and material worked, the number of finished pieces of work (e.g. cogwheels) which can be produced before the tool has to be reground, through becoming blunt, is determined. The greater the number of finished pieces produced under such comparable conditions the better the cutting oil (see Fig. 1).

The cutting action is influenced not only by the composition of the oil, but also to a considerable degree by its manner of application. The oil should overflow the cutting edge of the tool in a regular wide stream, adequately wetting both tool and work. The amount of oil introduced should not be less than 15–20 litres per minute, this amount being increased in accordance with the number of tools in use in the machine. Straight cutting oils—in contrast to water emulsions—should be used for difficult operations (four-spindle automatics, screw-cutting, &c.), and in cutting metals offering high resistance, such as the high alloy steels. Straight oils should also be used on principle in the case of automatics, milling machines, &c., where there is a danger that an emulsified oil, through overflow of the machine parts, may drive out the lubricating oil from the bearings and key grooves, thereby causing undue wear.

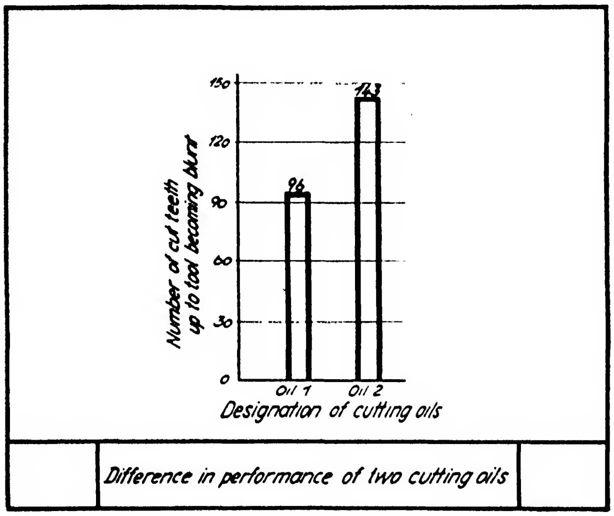
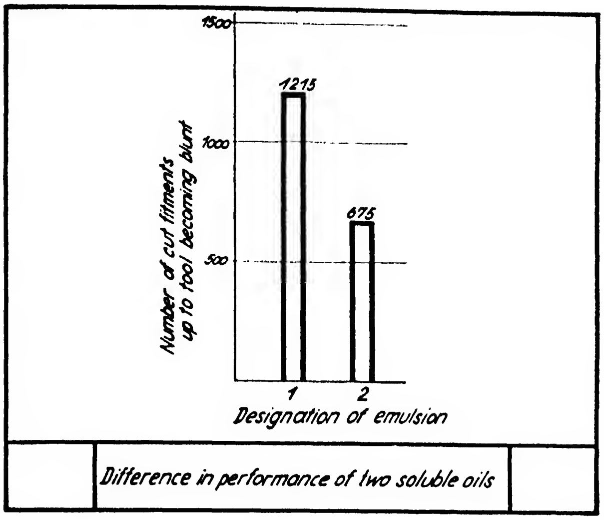


Fig. 1.

In many cases an oil emulsified with water (termed a 'water-soluble' oil, and sometimes a 'boring oil') is used in cutting operations. These oils consist for the most part of a solution of a soap in mineral oil, in which the total fat content should not be less than 80%. These oils are emulsified with water in the proportion of 1:10, or as required in stronger or weaker mixture. Their use is recommended when relatively light cutting operations are involved, and especially when great cooling capacity is required. Testing for suitability in the removal of cuttings is carried out in a similar manner to that of straight cutting oils (Fig. 2). Their capacity for emulsification with water and the stability of the emulsion is tested as follows: in a 1:10 solution of the oil in water no clear oil layer should separate after standing 24 hours at ordinary room temperature. Hard, lime-containing water is unsuitable for producing the emulsion. In such a case the water should be softened by the use of sodium carbonate in accordance with the following formulae:

1 German degree of hardness
≙ 10 mg. CaO (calcium oxide, quicklime) in 1 litre of water
≙ 18·9 mg. Na_2CO_3 (anhydrous sodium carbonate)
≙ 51 mg. $Na_2CO_3 \cdot 10H_2O$ (sodium carbonate crystals).

During its use in the machine the emulsion is continually losing oil, the oil tending to segregate on the metal surfaces to the exclusion of the water, and consequently periodic examinations must be made to observe whether the emulsion still contains sufficient oil. The testing flask, illustrated in Fig. 3, may be used, the emulsion to be tested being poured in as far as the lower graduation, and hydrochloric acid added to the upper graduation. The oil separates as a distinct upper layer, its percentage being read off directly from the divisions on the neck of the flask.



Difference in performance of two soluble oils

FIG. 2.

In the case of grinding operations a cooling liquid should be used containing a proportion of not more than 2% of a soluble cutting oil. The oil should emulsify particularly well if uniform and consistent emulsions are to be obtained with such small concentrations. With a higher proportion of oil, trouble may be experienced through clogging of the grinding wheels and through accumulation of sludge from the grinding dust.

In working cast iron and malleable cast iron emulsified boring oils are used exclusively, since the friable cuttings cannot be satisfactorily washed away when a straight cutting oil is used.

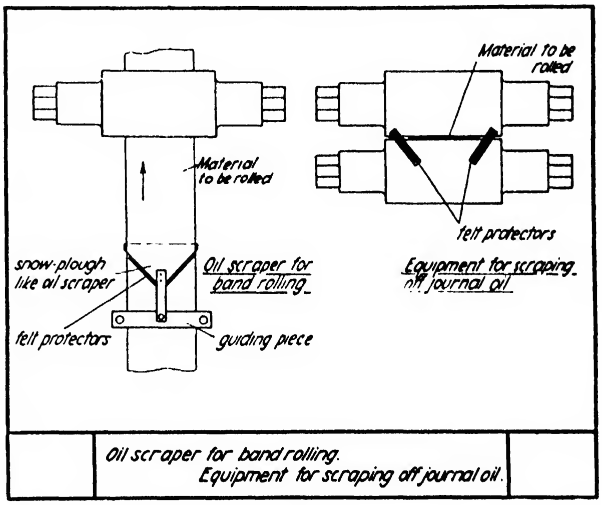
Class 2. Drawing and Pressing Oils

The cutting and boring oils described previously may also be used for such operations as wire-drawing, pressing, and cold rolling, in which no cuttings are detached, provided that no special demands are made. In this case also, fatty oils of animal or vegetable origin have the disadvantages pointed out in the previous section.

The suitability of wire-drawing oils, &c., is tested by comparative measurement of the force required in the drawing operation. For wires, &c., the force may be measured by means of ring-shaped gauge chambers. According to the experiments of Pomp and Koch, the relative efficiencies of fatty and mineral oils are such that, as in the case of cutting oils, there is no valid reason for preferring fatty oils.

Fats or greases are also used to a certain extent in drawing operations, as in the preliminary drawing of wires. There is no precise line of demarcation for the preferential use of a straight or of an emulsified oil for drawing. A straight drawing oil should be used in the case of highly resistant material and hard draws. In all other cases an emulsified oil will suffice. Such oils are mixed with water in the proportions of 1:1 up to 1:40, according to requirements. The working material and not the tool should be lubricated. In wire drawing, it is of particular importance that the lubricant used should have a high degree of oiliness.

In the cold rolling of steel and non-ferrous metals it is necessary that the work is wetted with a suitable lubricant during rolling. During cold rolling, one or more annealings of the material are generally necessary, and during such annealing unsuitable oils used in the rolling and remaining on the work tend to leave a residue, termed 'spill' (Fig. 4). The formation of this residue may be a source of considerable trouble, as in many cases it cannot be removed even by pickling. Therefore, to obtain a satisfactorily clean surface, oils must be used which leave no residue on ignition, and yet are sufficiently viscous to give satisfactory rolling. Such oils are known as 'bright-rolling oils'. It is in any case necessary to use the oil sparingly on the material to be rolled, since an appreciable residue is formed from clean-rolling oils if used in excessive quantity. To remove excess oil, the device shown in Fig. 5 may be used.



Oil scraper for band rolling.
Equipment for scraping off journal oil.

FIG. 5.

The increase in speed, and deformation, during the cold rolling process causes such pronounced heating that it may be necessary to cool the rolls and material. Straight oils are no longer satisfactory for this, and in such cases an emulsion with water having a much greater cooling capacity is used. Care must be taken that the oil content of the emulsion is maintained constant, the apparatus illustrated in Fig. 3 being used to observe any change.

In choosing suitable oils particular attention should be paid to the cleaning arrangements available, through which the material to be rolled should be passed before annealing.

In the lubrication of the roll bearings very viscous oils or fairly stiff greases are used, capable of resisting high bearing pressures. Such lubricants leave a pronounced residue on ignition, and great care must therefore be taken that the bearing lubricant cannot leak on to the rolls and contaminate the work. To prevent this, cotton waste may be applied to the rolls, but it is preferable to arrange the bearing construction and the lubricant application so that contact with the rolls is impossible.

Class 3. Quenching, Tempering, and Annealing Oils

In considering oils used in the heat treatment of metals, distinction is drawn between quenching and tempering oils and annealing oils.

In the case of quenching and tempering oils, account must be taken both of the heat transfer between the work and the bath liquid and of the change induced in the oil through frequent contact with the glowing steel and hot scale. A good tempering oil can be recognized by the interaction (between oil and steel). Until recently it was customary for traditional reasons to use animal or vegetable oils or mixtures of these with mineral oils. It has previously been pointed out in the case of cutting oils that fatty oils have a pronounced tendency towards deterioration on account of their chemical structure. This is far more pronounced in tempering operations during which the oil is continuously used at high temperatures, at which deterioration is most rapid. The following figures give some idea of the change in a rape-seed oil after 200 hours' use in a tempering bath:

Deterioration of Rape-seed Oil

Data	*Unused oil*	*Used oil*
Viscosity, ° E. at 20° C. . .	12·8	. .
„ „ 50° C. . .	4·20	23·9
Specific gravity . . .	0·915	0·941

In addition it was reported that the used oil showed a viscosity comparable with cylinder oil, with separation of a carbonaceous deposit and gelatinous sludge. The oil showed pronounced foaming, and it was impossible to give the correct hardness to the work.

The deterioration of tempering oils is still more pronounced when salt baths are used. In tempering processes salt baths are being used to an increasing extent as their advantages are more generally recognized. When the steel pieces, having been heated in the salt bath, are removed for chilling in the oil, a more or less considerable residue of salt always remains on the work. This layer of salt has the great advantage that air is excluded from contact with the surface of the work, so that oxidation is prevented. On the other hand, it has the disadvantage that at high temperatures the salt may enter into reaction with the tempering oil. An unsuitable oil, such as a fatty oil, is rendered useless through the consequent saponification. In addition the saponified layer adhering to the work is very difficult to remove. A mixture of fatty and mineral oils is similarly unsuitable here, for, corresponding to the proportion of fatty oil present, saponification caused by the salt sets in, with rapid deterioration of the oil.

In salt-bath tempering, therefore, only pure mineral oils should be used. The following simple test will indicate whether or not a pure mineral oil is involved. Unsaponifiable oils (such as pure mineral oils) are not attacked on heating with caustic potash. If, however, the oil contains even a small quantity of saponifiable matter, it will show an increase in viscosity, or even gelatinization, when heated in a test-tube with a small quantity of caustic potash.

A good tempering oil should have a viscosity of not less than 1·5° E. at 50° C., and a flash-point of not less than 140° C. Too much emphasis should not be laid on the flash-point, however, as fires may easily be caused when large pieces are placed in the tempering bath. Such fires may readily be extinguished by means of covering devices.

If too high a viscosity is chosen, the losses through adherence to the work, and through dripping, will be excessive when the work is removed from the oil bath. Apart from this it is a general rule that an oil chills more effectively the lower its viscosity. The chilling capacity of an oil may therefore be increased, to some extent, by raising its temperature, with resultant decrease in viscosity. The temperature used should not exceed approximately 100° C.

In many cases attempts have been made to use distillate oils in large tempering plants on account of their economy. Experiment has shown, however, that this procedure is not to be recommended. Cracking of the oil occurs upon introduction of the hot metal, which may lead to the production, at localized places, of the 'spheroidal state' at the oil/metal interface (Leydenfrost phenomenon). This, in turn, leads to uneven heat transfer, with possible production of localized strains, and lines of weakness in the work. In addition, increased loss of oil occurs with the cracking. The relatively large proportion of unstable constituents not removed by refining also causes excessive deterioration and sludging of these distillate oils.

Latterly, so-called 'non-sludging' oils (clean tempering oils) have been introduced to some extent. As their name implies, these non-sludging oils keep the tempered work as free as possible from adherent oil crust, with consequent retention of its clean surface. The use of such oils is, however, of little value if oxidation has already been allowed to take place during heating. Non-sludging oils are particularly important in salt-bath tempering, saponification being prevented and the condition of the surface of the work preserved. In addition it is found with such oils that the adherent layer of salt on the work scales off very readily in the tempering bath.

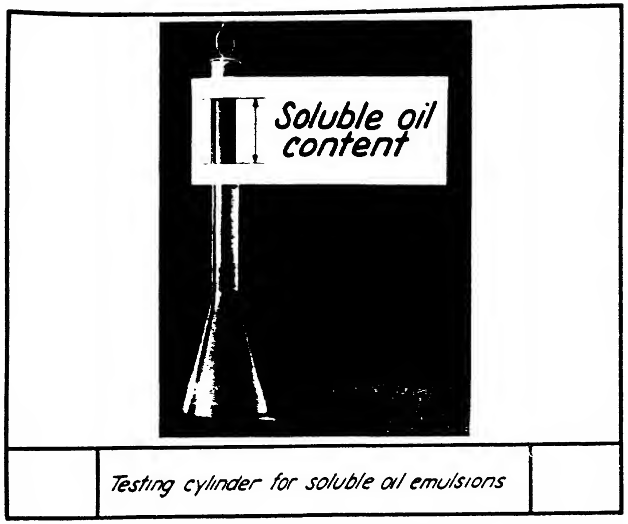
Oils used in large tempering plants require particular attention during working. It is always advisable to arrange for a satisfactory dipping procedure, to avoid localized overheating of the oil, and obtain rapid cooling. In certain circumstances it is even advisable to set up a stirring apparatus in the tempering bath, as more heat is led away from the work by efficient agitation than by excessive cooling. It is also advisable to arrange for filtration (preferably continuous) of the oil in a subsidiary circuit to remove scale and sludge.

If pipe coolers (using water cooling) are incorporated in the plant, the cooling water should be at a lower pressure than the oil flowing through, to diminish the possibility of water leakage into the tempering oil. The presence of water in a tempering oil leads to excessive foaming and violent spitting during the quenching operation. In such cases the water should be removed by careful evaporation, otherwise satisfactory tempering is impossible.

In general, the same oils are used for tempering as for quenching.

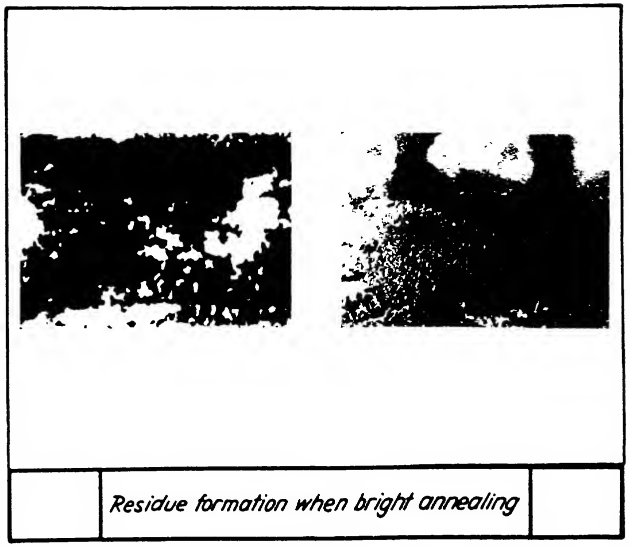
Annealing oils, as the name implies, are used to anneal tempered and other work. Here the flash-point of the oil is the chief factor determining the temperature at which the oil may be used. Since oils with a flash-point of over 350° C. are not available, the upper temperature limit for the use of an annealing oil is approximately 340° C. Above this temperature other annealing agents must be employed, such as salt baths, lead baths, &c. Particularly high demands are made on annealing oils, in so far as the bath is maintained at the annealing temperature over long periods. Because of their high flash-point, cylinder oils only are applicable. The viscosity should be not less than 2·5° E. at 100° C. and the flash-point not lower than 240° C. Oils should be used having the smallest possible asphalt content and the least possible tendency to form asphalt during service. The analytical data of an oil, however, do not always give an adequate picture of its behaviour in practice, and should be supplemented by practical experiment.

In annealing operations where temperatures of 220° C.



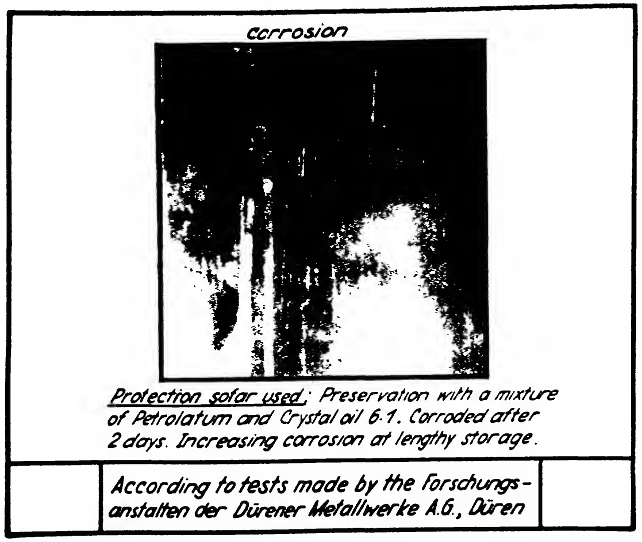
Testing cylinder for soluble oil emulsions

FIG. 3



Residue formation when bright annealing

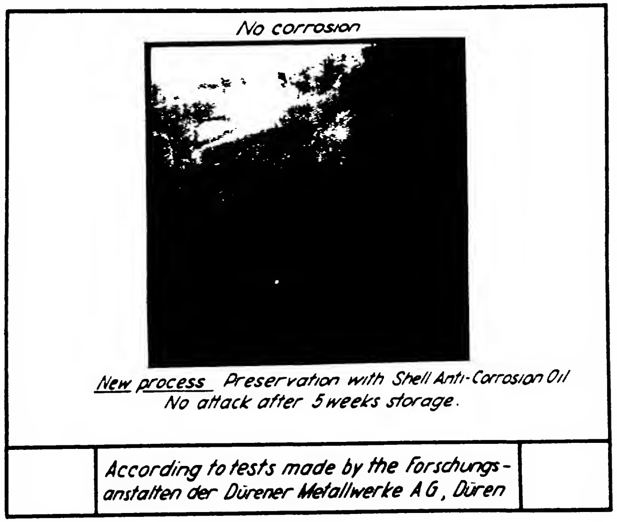
FIG. 4



Protection sofar used: Preservation with a mixture of Petrolatum and Crystal oil 6·1. Corroded after 2 days. Increasing corrosion at lengthy storage.

According to tests made by the Forschungsanstalten der Dürener Metallwerke A.G., Düren

FIG. 6



New process Preservation with Shell Anti-Corrosion Oil No attack after 5 weeks storage.

According to tests made by the Forschungsanstalten der Dürener Metallwerke A G, Düren

FIG. 7

are not exceeded, it is preferable to use a non-sludging type of oil.

Class 4. Anti-corrosion Oils

It is often necessary to protect the parts which have been tempered against subsequent corrosion. This is particularly important in the case of salt-bath tempering, when care is not always given that the salt residue is thoroughly washed away during immersion in the tempering bath; it is then necessary to follow with a vigorous spray of hot water for final cleansing. To protect the work against subsequent corrosion, containers are set up in the salt-bath tempering plant which are filled with so-called anti-corrosion oils. These oils are used in the form of an emulsion with water, in the proportion of 1 : 10. The parts to be protected are simply dipped into this mixture and, after the water has been evaporated off, a thin but tenacious film of oil is left behind which affords protection against all kinds of corrosion. If the material is to be stored away for a considerable period, the protection process should be repeated from time to time.

Recently another kind of protective process has assumed importance. The finished rolled material (steel, light metal, &c.) which is subsequently to be used in the production of tins or wrapping bands is liable to excessive corrosion through condensation of moisture. Such condensation, caused by differences of temperature and weather, cannot be controlled and some form of protective coating is essential. Formerly this was supplied by fatty oils or vaseline, but, as shown by experiments at the Duren metalworks (Fig. 6), no satisfactory degree of protection against such corrosion is given by vaseline or mixtures of fatty oils, the moisture penetrating through the protective layer and still causing corrosion. The most satisfactory form of protection is found to be an oil capable of self-emulsification (English Pat. no. 408,896). This oil neutralizes the effect of any condensation which may have taken place as well as any formed later. Fig. 7 shows that no corrosion appears even after several weeks' storage.

The application of this anti-corrosion oil may be either by hand or by means of spraying guns. When applied by hand, the addition of 10% of kerosine is recommended in order to give a mixture of good covering capacity. Such an addition does not harm the action of the oil. When using spraying guns it is advisable to make use of spraying tables which facilitate application of the oil and automatically recover any surplus of oil applied. In the case of strip metal which is subsequently to be rolled it is advisable to undertake the preserving process during rewinding. The anti-corrosion oil is equally suitable for steel and non-ferrous metals. In many cases it is desirable to maintain a particularly strong and tenacious film protective on the work. Approximately 10–25% of a viscous mineral oil should be mixed with the anti-corrosion oil, its capacity for self-emulsification being not harmed thereby.

Class 5. Oils for Blackening Steel and Iron Surfaces

When necessary to improve the surface of machine parts by blackening, and in addition to protect them from rusting, some form of chemical treatment has been adopted in the past, a procedure both costly and difficult to operate. Alternatively, machine oil was applied to the heated parts and subsequently burnt slowly off. This operation is unpleasant for the workers, owing to the heavy smoke formed, and it is difficult to ensure even burning-in of the oil on the surface treated. Latterly it has been found that an emulsion of a suitable oil with water is particularly satisfactory. The heated parts are dipped in the emulsion and cooled; after cooling they are removed. Through vaporization of the water content of the emulsion a thin film of the emulsified oil remains and is subsequently burnt into the surface of the material. The finished work has a fine, regularly black appearance and resists rust well. This process is distinguished by its economy, as in the circumstances the addition of only 2–3% of oil to the water is necessary. The choice of the oil is of importance, for only an oil with a very strong fat basis can be used. It is also important to maintain the proportion of oil in the emulsion exactly. For this purpose the same apparatus shown in Fig. 2 may be used.

When metal cutting oils are used, trouble is sometimes caused through skin disease contracted by the workers. Such phenomena are present to some extent with all mineral and fatty oils, and in addition certain persons are particularly sensitive to them. In most cases the infection is started through small skin wounds caused by the mechanism operated or by the metal cuttings. In many cases workers do not pay sufficient attention to skin cleanliness. The British Government has published a pamphlet dealing with the desirable preventative and protective measures (no. 397, London, H.M. Stationery Office), and it is strongly recommended that factories should follow the measures outlined in this pamphlet.

SELECTED BIBLIOGRAPHY

Bericht Nr. 25 des Schweiz. Verband f. d. Materialprüfungen der Technik, Zürich.

BOSTON, O. W., GILBERT, W. W., and KRAUS, C. C. The Influence of Cutting Fluids on Tool Life in Turning Steel. *Trans. Amer. Soc. Mech. Eng.* 7, 36, p. 371.

KREKELER, K. *Öl im Betrieb, Werkstattbuch*, Heft 48, Verlag Jul. Springer, Berlin.

KRELELER und RAPATZ. Beitrag zur Frage der in Wärme-behandlungsbetrieben zu verwendenden Öle. *Archiv f. d. Eisenhüttenwesen*, **5**, 1931, Heft 3, Ss. 173–6.

POMP und KOCH. Über d. Einfluss d. Schmiermittels auf d. Kraftbedarf beim Ziehen u. Flusstahldraht mit Krupp-Widia-Ziehsteinen. *Mittlg. d. KWI-Düsseldorf*, Bd. **13**, 1931 (Liefrg. 22).

SYNTHETIC LUBRICATING OILS

By F. C. HALL, Ph.D., A.I.C., A.M.Inst.P.T.

Department of Oil Engineering and Refining, University of Birmingham, England

ALTHOUGH the extent of natural petroleum resources appears adequate to supply the demand for lubricating oils for many years, a considerable amount of research has been and is being carried out on their synthetic production. This may partly be attributed to economic conditions, particularly in the case of those countries with no indigenous sources of petroleum, and also to the possibility of synthesizing lubricants of higher grade or of more specialized characteristics than those now available. At the present time the trend is almost entirely in the direction of employing lubricating oils of predominantly hydrocarbon constitution, although non-hydrocarbon oils, such as fatty oils, continue to be used to a small extent. It would appear that this preference for hydrocarbon lubricants is likely to persist, with an exception made in the use of relatively small proportions of blending materials for improving oiliness, oxidation, stability, or other properties of the oil. This article is therefore confined to the synthesis of hydrocarbon lubricating oils. Before discussing the methods available for these syntheses, brief attention will be given to the constitution of petroleum lubricants.

Chemical Structure of Lubricating Oils

The relationship between viscosity and other properties of hydrocarbon oils and their chemical structure has received increasing attention of recent years, culminating on the analytical side in Research Project No. 6 of the American Petroleum Institute [72, 1935], now in progress, and on the synthetic side in the syntheses of high molecular weight hydrocarbons of known constitution by several investigators, including Hugel [36, 1931–2], Lerer [55, 1933], Landa [54, 1933–4], and Mikeska [60, 1936]. From the accumulated data now available, particularly those from the hydrocarbon syntheses, the general relationship of chemical structure to some of the more important properties of lubricating oils can be very briefly summarized as follows:

Petroleum lubricating oils are composed of an extremely complex mixture of hydrocarbons whose molecular constitution may contain cyclic, polycyclic, and open-chain structures. The relative proportion, character, and structural positioning of these groupings largely determine the general physical and chemical properties of the oil, regarded as a whole. Open-chain—paraffinic—structure is associated with low viscosity, high viscosity index, low specific gravity, and high setting-point. Branching of the open-chain groupings leads to a lowering of the setting-point and viscosity index, while the introduction of cyclic structure increases the viscosity and specific gravity. With growing complexity of the ring structure the viscosity is very markedly increased, and the viscosity index diminished. The reduction of aromatic groupings to naphthene rings raises the viscosity with but little alteration in the viscosity index.

The hydrocarbon constituents of paraffin-base lubricating oils appear, then, to have long open chains associated with relatively simple rings; with decreasing proportion of open-chain to cyclic structure, and increasing complexity of the cyclic nuclei, the naphthene- and asphalt-base oils are approached, having low viscosity indices and high specific gravities. The correlation of these physical properties is further complicated, in the case of lubricating oils, by the colloidal characteristics exhibited by solutions and liquid mixtures of these high molecular weight components. Particularly is this the case with regard to viscosity, viscosity temperature, and setting-point phenomena. The question of stability towards oxidation, of extreme importance in the case of modern automotive lubricants, is intimately connected, not only with the general chemical constitution of the oil, but with the presence or absence of inhibiting or catalytically active components.

Table I, adapted from Rossini, illustrates the marked influence of chemical structure upon physical characteristics by reference to synthesized hydrocarbons.

For a more detailed account of these factors the reader is referred to papers by Hugel [36, 1932], Rossini [72, 1935], Wiggins [85, 1936], and particularly to a recent publication by Mikeska [60, 1936], describing the syntheses, properties, and correlation of properties with structure for 52 hydrocarbons of high molecular weight.

Methods Available for the Synthesis of Lubricating Oils

Regarding the synthesis of lubricating oils as being essentially a means of building up hydrocarbon molecules of a size comparable with those present in petroleum lubricants, the principal methods available for such syntheses may be summarized as follows:

1. Non-catalytic polymerization of hydrocarbons.
2. Catalytic polymerization of hydrocarbons.
3. Dechlorination of chlorinated hydrocarbons.
4. Condensation of olefinic with aromatic hydrocarbons.
5. Condensation of chlorinated hydrocarbons with aromatics.

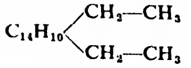
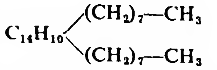
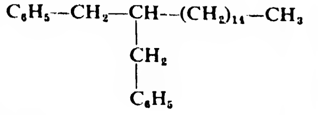
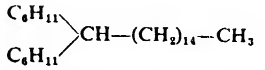
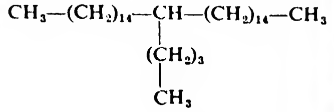
By reason of their unsaturated and reactive nature, olefinic hydrocarbons are particularly applicable to polymerization and condensation reactions. In the case of the less reactive saturated hydrocarbons, reactivity may be achieved through the preliminary or intermediate formation of an unsaturated hydrocarbon and its subsequent polymerization or condensation to a more complex molecular condition. This may be carried out through a dehydrogenation reaction, as by electrical treatment with the silent discharge, or by chlorination of the initial material followed by dechlorination and production of an unstable intermediate.

Non-catalytic Polymerization by the Silent Electric Discharge

The silent electric discharge, as in the Siemens ozonizer, causes polymerization of olefinic and saturated hydrocarbons to compounds of widely varying molecular complexity [62, 1934]. Investigation of the reaction in the case of the simpler gaseous hydrocarbons by Saint-Aunay [73, 1933] indicates that the following basic reactions may proceed: dehydrogenation followed by polymerization

TABLE I

Synthetic Hydrocarbons of High Molecular Weight

Hydrocarbon	*Structure*	*Type*	*Molecular weight*	*Viscosity at 100° F., centistokes*	*Viscosity index*	*Density, d_4^{20}*
Di-hydro-diethyl-anthracene $C_{18}H_{20}$	 $C_{14}H_{10}\begin{matrix}\diagup CH_2-CH_3\\ \diagdown CH_2-CH_3\end{matrix}$	polycyclic-aromatic	236	35·7	−390	1·014
Di-hydro-dioctyl-anthracene $C_{30}H_{44}$	 $C_{14}H_{10}\begin{matrix}\diagup (CH_2)_7-CH_3\\ \diagdown (CH_2)_7-CH_3\end{matrix}$	polycyclic-aromatic-paraffinic	404	293	−9	0·948
Phenyl-benzyl-heptadecane $C_{30}H_{46}$	 $\begin{array}{l}C_6H_5-CH_2-CH-(CH_2)_{14}-CH_3\\ \qquad\qquad\quad\;\; \vert\\ \qquad\qquad\quad\; CH_2\\ \qquad\qquad\quad\;\; \vert\\ \qquad\qquad\quad\; C_6H_5\end{array}$	simple-aromatic-paraffinic	406	34·5	85	0·917
Di-cyclohexyl-hexadecane $C_{28}H_{54}$	 $\begin{matrix}C_6H_{11}\diagdown\\ C_6H_{11}\diagup\end{matrix}CH-(CH_2)_{14}-CH_3$	simple-naphthenic paraffinic	390	32·9	98	0·879
n-Butyl-hentriacontane $C_{35}H_{72}$	 $\begin{array}{l}CH_3-(CH_2)_{14}-CH-(CH_2)_{14}-CH_3\\ \qquad\qquad\qquad\quad\;\; \vert\\ \qquad\qquad\qquad\quad (CH_2)_3\\ \qquad\qquad\qquad\quad\;\; \vert\\ \qquad\qquad\qquad\quad\; CH_3\end{array}$	paraffinic	492	25·2	151	0·824

and hydrogenation by the liberated hydrogen; decomposition of the molecule, and polymerization of unsaturated molecules. These primary reactions are complicated by the subsequent action of the discharge upon their initial products.

Ethylene and other gaseous hydrocarbons yield unsaturated liquids of characteristics dependent upon the experimental conditions. Prolonged action of the discharge leads to products of high molecular weight, and Epner [18] has claimed that lubricating oils can be obtained in this manner from methane, ethylene, and similar hydrocarbon gases.

The action of the discharge upon liquid hydrocarbons and fatty oils, particularly in the presence of hydrogen at reduced pressure, leads to an increase in the viscosity of the oil and improvement of the viscosity temperature characteristics. It is considered that hydrogen is split off under electronic bombardment, with resultant polymerization of the unsaturated residues and hydrogenation by the liberated hydrogen, the products having a higher molecular weight and degree of saturation [62, 1934]. This reaction has been utilized in the Voltol and Electrion [71, 1930] processes for the production of lubricants. In the Voltol process, described by Otto [67, 1931] and Wolf [86, 1929], fatty oils are subjected to alternating current at 4,000–5,000 volts and 500 frequency, at temperatures up to 80° C., the products being blended with straight petroleum oils.

The production of voltolized petroleum oils and their utilization as blending stock for increasing viscosity index and depressing pour-point has recently been discussed by Woods [87, 1936]. Using a blend of 50% crude scale wax (120° F. m.p.) and 50% waxy Mid-Continent overhead oil as charging stock, a power consumption of 15 K.W.H. gave a 10% yield (after vacuum distillation and recycling light overhead) of voltolized oil with the properties (after dewaxing and clay treatment) given in Table II.

After a power consumption of 60 K.W.H. a yield of 57% of a very viscous oil was obtained, a 10% blend of which with a finished Mid-Continent paraffin-base motor oil raised the viscosity index to 119. A 5·0% blend with a paraffin-base oil was stated to reduce the pour-point from 30 to −15° F.

TABLE II

Properties of Voltolized Oils

Oil	*Viscosity, 100°F.*	*Saybolt Universal, 210°F.*	*Viscosity index*	*Sp. gr. 60/60°F.*	*Pour-point, °F.*
Voltolized oil (15 K.W.H.) .	1,105	121·7	123	0·864	15
After 60 K.W.H. .	..	349·4	..	0·867	70
10% blend with Mid-Continent oil .	413	64	119	0·880	0
Original Mid-Continent oil . .	387	56·3	90	0·881	10

This process is applicable also to low-temperature coal and lignite tars and their fractions [17, 1923], and has been used for the treatment of synthetic lubricating oils from condensation reactions [41]. Schildwächter [75, 1934] has described the effect of voltolization upon fractions from the condensation of ethylene with aromatic hydrocarbons and oils.

Catalytic Polymerization of Unsaturated Hydrocarbons

The polymerization of unsaturated hydrocarbons is accelerated to a marked degree by catalytic action. A wide range of catalytic materials is available for this purpose, including phosphoric and sulphuric acids, a number of volatile inorganic halides (the Friedel-Crafts type of catalyst) such as boron trifluoride and chlorides of aluminium, zinc, tin, titanium and phosphorus, and active bleaching earths. For a more detailed account of polymerization catalysts reference should be made to 'Pyrolysis and Polymerization Processes for the Production of Liquid Fuel from Gaseous Hydrocarbons' by D. A. Howes. The majority of these catalysts appear to function through the intermediate formation of a comparatively unstable compound of the unsaturated hydrocarbon and the catalytic substance, followed by its decomposition with regeneration of the catalyst and production of polymerized hydrocarbons.

In the synthesis of high molecular weight hydrocarbon oils suitable for lubricants, aluminium chloride and boron trifluoride catalysts have been investigated in some detail, their activity enabling a high degree of polymerization to be obtained with short reaction periods. The polymerization of ethylene under pressure in the presence of aluminium chloride was observed by Ipatieff [45, 1911], and later by Ipatieff and Routala [49, 1913], and Szayna [81, 1928], and has been described in detail by Stanley [79, 1930; 64, 1930], with particular reference to the value of the lubricating-oil fractions. The conclusions drawn may be summarized as follows:

At normal temperatures, using ethylene under pressure, the products of the reaction comprise a 'free oil' of purely hydrocarbon nature, together with a pasty 'double compound' of aluminium chloride and a so-called 'combined oil' of olefinic character which could be liberated from the double compound by the action of water. The double compound [30, 1916–17] represents an intermediate stage in the polymerization of the ethylene to the stable-free oil, being itself an active catalyst for polymerization [43, 1929].

The free oil, upon distillation, yields a range of fractions, of general composition C_nH_{2n}, the higher boiling approximating in general characteristics to petroleum lubricants. These oils, while of stable and saturated character, have poor viscosity indices, while the high-boiling residual fractions were extremely viscous. The specific gravities of these fractions are remarkably low.

Raising the temperature of reaction increases the rate of polymerization to a very marked extent, but leads to a shortened life for the catalyst and considerable alteration in the character of the products obtained. The polymerizing action of aluminium chloride at higher temperatures is complicated by its pronounced tendency to initiate cracking and dehydrogenation reactions [24, 1924; 48, 1936], giving rise to an increased proportion of low-boiling paraffin hydrocarbons with simultaneous formation of heavy polycyclic hydrocarbons, of composition C_nH_{2n-6} to C_nH_{2n-10}, having a high carbon hydrogen ratio. The lubricating fractions, as a result, exhibit still more pronounced naphthenic and aromatic properties, with very steep viscosity temperature curves and relatively high specific gravities. These fractions possess a much higher viscosity for a given boiling range or molecular weight than normal petroleum lubricants. At higher temperatures the aluminium chloride double compound becomes more carbonaceous, and of considerably reduced catalytic activity.

The characteristics of typical lubricating fractions from the polymerization of ethylene are shown in Table III. The oxidation stability of these oils is in general lower than that of petroleum lubricants, although sludge formation is small, the oils produced at lower temperatures being more stable. The lubricating oils obtained at differing temperatures by aluminium chloride polymerization of technically available ethylene concentrates have been described by Petrov, Antzuz, and Pozhiltzeva [69, 1933].

The mechanism of the polymerization has been discussed by Stanley [79, 1930; 64, 1930], Hunter and Yohe [37, 1933], Ipatieff [46, 1936], and others.

Recently it has been shown by Hall, Wiggins, and Nash [82, 1935] that the polymerization reaction at relatively high temperatures is considerably modified by the presence of metallic aluminium. The formation of low-boiling hydrocarbons is reduced, the lubricating oil fractions have viscosity indices as high as 50 to 70 and the formation of a carbonaceous aluminium chloride complex is prevented. The aluminium chloride is, in the presence of ethylene and aluminium metal, transformed into compounds of true organo-metallic nature resembling, in some respects, the Grignard compounds of magnesium, and showing marked activity towards oxygen and water. The properties of two lubricating oil fractions are included in Table III.

TABLE III

Lubricating Oils from the Polymerization of Ethylene

Catalyst	*Polymerization temperature, ° C.*	*Viscosity at 100°F., centistokes*	*Viscosity index*	*Sp. gr. 60/60°F.*
Aluminium chloride .	15	112*	−30*	0·836
,, ,, .	150	200*	−230*	0·921
Aluminium + aluminium chloride† . . .	200	1,610	67	0·902
Aluminium + aluminium chloride . . .	300	217	40	0·890
Boron trifluoride . .	low temperature	133‡	45‡	..

* Calculated from Stanley's data.
† Data given for a viscous residual oil.
‡ Calculated from Otto's data.

At higher temperatures (250–300° C.) the organo-metallic compound—inert at lower temperatures—becomes catalytically active and considerable yields of liquid olefines, including butene, hexenes, and octenes, are obtained [27, 1937]. These olefines can then be polymerized in a second stage to give lubricating-oil fractions of high viscosity index. At low temperatures, the addition of finely powdered zinc or aluminium has been stated to increase the yield of free oil in the aluminium chloride polymerization of ethylene [34, 1931].

The use of aluminium chloride and other inorganic halides in combination with organic polar compounds (nitrobenzene for example) and with inactive metallic halides such as sodium chloride, for the polymerization of gaseous olefines has been claimed by Elkington [6, 1931], while Howes has suggested the use of florida earth impregnated with aluminium chloride [35, 1932].

The polymerization of ethylene and other olefines by the action of boron trifluoride has been described by Otto [66, 1927]. It was found that ethylene under a pressure of 70 atm. could be polymerized by boron trifluoride at ordinary temperatures with the formation of viscous oils of empirical formula C_nH_{2n}. At higher reaction temperatures the viscosity of the crude hydrocarbon mixture was found to diminish rapidly. The higher fractions were described as being comparable with petroleum lubricants as regards viscosity temperature relationship, and the properties of a typical oil are included in Table III.

Hoffman, Otto, and Stegemann [32, 1928–9] suggest the polymerization of olefines under pressure by the use of boron trifluoride in the presence of water, halogen acids, or halogenated hydrocarbons capable of reacting with benzene in the Friedel-Crafts synthesis. In another patent [31, 1927, 1931] the addition of finely powdered metals, especially nickel, is claimed to accelerate the polymerization. It is of interest to note that the boron trifluoride used for polymerization may be practically completely regenerated from the reaction products by the action of heat.

Polymerization of Higher Olefines

The properties of the oils produced by polymerization are dependent to a considerable degree upon the type of olefinic material used for the reaction. The more highly unsaturated, less stable, diolefines have been shown by Thomas and Carmody [83, 1932] to yield resinous polymers. The polymerization of the higher olefines to lubricating oils has been investigated in detail by Sullivan and collaborators [80, 1930–1, 1934], their work being described in detail in 'The Manufacture of Synthetic Lubricating Oils', p. 2664. Their results lead to the following general conclusions: Cyclic olefines, such as cyclo-hexene and dipentene, were found to yield polymerized oils with extremely poor viscosity indices. Among open-chain olefines, the homologues of ethylene were polymerized more readily than ethylene itself, and the lubricating properties, particularly the viscosity indices, of the resultant oils were found generally to improve with increasing chain-length of the initial olefine. Polymerized oils obtained from cetene—with a 16-carbon atom chain—had viscosity indices as high as 138, considerably higher than the values for petroleum lubricants. Branched-chain olefines gave polymerized oils of poorer viscosity temperature characteristics than the corresponding normal compounds. The constitution of lubricating fractions from the polymerization of isomeric pentenes has been described in detail by Waterman and others [84, 1935–6].

These factors are of considerable importance in the selection of olefinic materials for polymerization to lubricating oils by the action of aluminium chloride. Thus the polymerization of a cracked naphthenic or aromatic stock may yield oils of viscosity index lower than −100, whereas those from a cracked paraffinic stock have values of the order of 100.

Sullivan and collaborators have used cracked wax-bearing stocks for large-scale production of lubricating oils having high viscosity indices and oxidation stability, and the engine testing of these products has been described by Barnard [3, 1931–2].

The effect of increasing molecular weight of the olefinic stock polymerized is illustrated in the following table summarizing the properties of lubricating oils synthesized by Fischer from 'kogasin' fractions [19, 1935; 21, 1934]. Using a high carbon monoxide-hydrogen ratio and a catalyst of low nickel content, the lower boiling fractions of the synthetic kogasin contain considerable amounts of open-chain olefines. These were polymerized with aluminium chloride and the lubricating oils recovered by distillation.

TABLE IV

Oils from the Polymerization of 'Kogasin' Fractions

Boiling range of 'kogasin' fraction used, ° C.	*Olefines, vol. %*	*Polymerized oil*		
		*Viscosity at 100°F. in centistokes**	*Sp. gr. 60/60°F.*	*Viscosity index**
0–100	39	67	0·838	5
100–150	27	65	0·839	35
150–200	18	51	0·838	75
200–250	11	21	0·830	100

* Calculated by extrapolation from Fischer's data.

The polymerization of ethylene and low molecular weight olefines may be carried out in two stages, so that a product of comparatively high molecular weight is used for final polymerization. Atkinson and Storch [2, 1934] converted ethylene into a highly unsaturated light oil by thermal treatment at 370° C. and 70 atm. pressure, and by further polymerization with aluminium chloride at room temperature obtained residual lubricating-oil fractions with viscosity indices ranging from 50 to over 100. At the Fuel Research Board [16, 1936] it has recently been found that oils having viscosity indices ranging from 30 to 90 can similarly be obtained from ethylene by a preliminary polymerization at 350° C. with a molybdic oxide catalyst, followed by polymerization with aluminium chloride at 60° C.

In the case of gaseous and low-boiling olefines, the polymerization reaction is facilitated by the presence of a liquid diluent to improve contact between catalyst and reactants. An early patent of Allenet [1, 1923] covers the production of lubricating oils by passage of olefine gases into a (20%) suspension of aluminium chloride in light petroleum at ordinary temperatures and a pressure of 3 atm. Under these conditions condensation of the olefines may also take place with aromatic, naphthene, and even paraffinic hydrocarbons present in the diluent. Particularly is this the case when higher boiling 'middle' oils are used of relatively aromatic constitution, such as coal-tar distillates [53, 1928].

The polymerization of the unsaturateds in cracked spirits has been used as a means of refining, and for the production both of synthetic resins and of lubricating oils. Brownlee's process [13, 1918] for the manufacture of synthetic lubricating oils was based on the polymerization of liquid olefines in cracked spirits with aluminium chloride, while a more recent patent [10, 1932] suggests the use of a preliminary light refining treatment prior to the main polymerization.

The lubricating fractions obtained by treatment of low-temperature carbonization spirits have been examined at the Fuel Research Board laboratories [15, 1934]. The gas spirit obtained by scrubbing the gases from the carbonization of coal at 650° C., after soda and acid washing, was polymerized with 7% aluminium chloride at 78° C. for 12 hours and the lubricating fractions recovered by distillation. The viscosity indices of these products were low (11 to −195) and oxidation stability, except in the lightest fractions, was relatively poor. These oils contain a considerable proportion of condensation products arising from the aromatic constituents of the crude spirit, and it is questionable whether good lubricating oils can be produced from basic materials of this character. The polymerizing and condensing action of aluminium chloride has also been utilized in the production of lubricating oils from low-temperature coal tars and tar fractions [39].

Production of High Molecular Weight Polyermized Products

A recent development in polymerization reactions has been in the production of hydrocarbon polymers of very high molecular weight. Under controlled conditions, certain olefinic hydrocarbons (including styrene, butadiene, isobutylene) yield polymers having a degree of polymerization of the order of 1,000 or more. In suitable solvents these polymeric hydrocarbons give solutions of pronounced colloidal properties. The relatively low change in viscosity with temperature, characteristic of such solutions, is of particular interest in connexion with synthetic lubricating oils [57, 1934], and the high viscosity indices of Voltol and Electrion oils, for example, may partly be attributed to the colloidal dispersion of the molecular complexes formed during the electrical treatment.

The properties of 'Exanol' polymers have recently been described by Otto, Miller, Blackwood, and Davis [68, 1934] who state that by blending with 5% of such a product, the viscosity index of a Coastal lubricating-oil stock may be raised from 25 to a value of 110, with, however, a considerable increase in the viscosity. Data for typical blended oils are given in Table V. The production of these hydrocarbon polymers is described in a recent patent [77, 1935]. Low-boiling olefinic fractions—particularly those containing isobutylene—are polymerized at low temperatures with, for example, boron trifluoride. By fractional precipitation with solvents polymers of molecular weight up to 5,000–6,000 may be separated and utilized for blending purposes. The I.G. Farbenind. A-G. claim the production of polymerides of isobutylene having a molecular weight as high as 40,000 by polymerization at −80° C. with boron trifluoride [44, 1934].

TABLE V

Blending Properties of 'Exanol' Polymers

Oil	Viscosity Saybolt Universal at 100° F.	Viscosity Saybolt Universal at 210° F.	Viscosity index
Coastal distillate . . .	358	49·2	26
„ „ +1·5% exanol .	627	66·0	80
„ „ +5·0% exanol .	1,851	147·5	111

Dechlorination of Chlorinated Hydrocarbons

The chlorination of paraffin hydrocarbons, particularly in the case of petroleum distillates, proceeds smoothly at moderate temperatures, either in the gaseous or liquid phase, leading to mixtures of mono-and poly-chloro derivatives of varying complexity. Dechlorination—usually the removal of chlorine in the form of hydrogen chloride—may be carried out by thermal or catalytic treatment, and is generally followed by a varying degree of condensation and/or polymerization of the resultant unsaturated residues. By selection of reaction conditions, the products of dechlorination range from highly unsaturated materials to stable saturated oils. For the higher chlorinated paraffins, thermal dechlorination proceeds smoothly and to practical completion at temperatures below 200° C. Gardner and Bielouss [23, 1922; 74, 1920] found that under these conditions the dechlorination products of chlorinated middle oils could be utilized as drying oils, having highly unsaturated characteristics.

Tanaka and collaborators [82, 1933–4] using chlorinated paraffin waxes [22, 1933] have shown that by control of the degree of chlorination and the conditions of thermal dechlorination, viscous oils of practically saturated character can be obtained. The properties of two oils are summarized in Table VI, from which the low pour-point and high viscosity index can be seen.

TABLE VI

Lubricating Oils from the Thermal Dechlorination of Chlorinated Paraffin Wax

Chlorine content of chloroparaffin	Properties of oil from thermal dechlorination: Sp. gr. 60° F.	Viscosity at 100° F., centistokes	Viscosity index	Pour-point, ° F.
40	0·904	113	120	below −5
50	0·935	880	100	below −5

Using chloroparaffins of lower chlorine content, Hall, Wiggins, and Nash [28, 1935] find the products to have good viscosity indices, but very high carbon residues and dark colour.

By reaction with alkali, or other metals having a high affinity for halogens, dechlorination is achieved at lower temperatures, in a manner comparable with the Wurtz synthesis. Friedel and Crafts in 1877 observed the formation of oily polymers from amyl chloride by treatment with aluminium, and the reaction has latterly been utilized in the synthesis of lubricating oils. Fischer, Koch, and Wiedeking [21, 1934; 51, 1935] have described the preparation of lubricating oils from the action of activated aluminium at 130° C. upon chlorinated fractions of 'kogasin' from the low-pressure carbon monoxide-hydrogen synthesis. The resultant oils, after a bleaching-earth treatment and vacuum distillation, had high viscosity indices, relatively low viscosity, and were stated to possess good oxidation stability. The properties of typical dechlorination oils are given in Table VII.

TABLE VII

Lubricating Oils from the Catalytic Dechlorination of Chlorinated 'Kogasin'

Initial material	Sp. gr. 60/60° F.	Viscosity at 100° F., centistokes*	Viscosity index*
Monochloro kogasin . .	0·860	65	105
Dichloro kogasin . . .	0·877	100	105

* Calculated by extrapolation from Fischer's data.

In addition to activated aluminium, these investigators found the aluminium chloride complex separated from the reaction products to be an active and satisfactory dechlorination catalyst. In these catalytic dechlorination processes, the reaction is further complicated by the pronounced catalytic activity and cracking action of aluminium chloride formed *in situ* during the dechlorination. Aluminium chloride is an active catalyst for dechlorination, and its action on chlorinated coal-tar fractions has been claimed to give rise to oils of lubricating character [40, 1929].

Condensation of Olefines with Aromatic Hydrocarbons

By a modification of the Friedel-Crafts reaction, olefines may be condensed with aromatic hydrocarbons in the presence of suitable catalysts of the Friedel-Crafts type. Condensation can be effected either in the vapour or liquid phase, under normal or increased pressure, using a wide range of catalysts, including aluminium chloride, boron trifluoride [46, 1936], sulphuric acid [11, 1893], phosphoric acid [46, 1936], and activated bleaching earths [38, 1928]. The direct combination of ethylene and higher olefines with benzene and its homologues has been described by several workers [61, 1922, 1927]; Bodroux [8, 1929] has shown that cyclohexene may be condensed with simple and polynuclear aromatics, while recently Ipatieff and others [47, 1935] have extended the reaction to the condensation of olefines with both paraffin and naphthene hydrocarbons. The latter investigators also find that alkylation of aromatic hydrocarbons by paraffins is possible under suitable conditions [26, 1935].

The condensation products of naphthalene and other polycyclic hydrocarbons with olefines are viscous oils which may be utilized as lubricants, and the production of such alkylated naphthalenes is described in a series of patents by

Michel [58, 1926–7, 1930]. In the synthesis of lubricating oils by the condensation of ethylene and naphthalene under pressure, at temperatures of the order of 250°, using aluminium chloride, Howard [33, 1933] found that the oils were of pronouncedly aromatic character with very high viscosities for a given boiling range and very poor viscosity indices (of the order of −100). Similar products have been described by Schildwächter, from the condensation of ethylene with naphthalene, tetra-hydronaphthalene, and coal-tar fractions [75, 1934]. Condensations of this nature are rendered more complex through direct polymerization of the olefines, in addition to their condensation with aromatics.

Krauch [53, 1928] has pointed out that by the passage of olefinic gases into suspensions of aluminium chloride in middle oils, viscous oils are produced through condensation with the aromatic hydrocarbons present, and several patents cover reactions of this type [9, 1927–34]. Michel [59, 1928] has proposed that an Edeleanu extract should be used as the aromatic component in this class of reaction, while a recent patent [4, 1936] claims the production of lubricating oils from the condensation of acetylene with aromatic hydrocarbons in the presence of aluminium chloride.

It can be concluded that lubricating oils synthesized by condensation reactions of this type possess a high proportion of aromatic structure in their molecular constitution, and may, in general, be expected to have poor viscosity indices, with a high viscosity and specific gravity for a relatively low-boiling range.

The Production of Lubricating Oils by the Condensation of Alkyl Chlorides with Aromatic Hydrocarbons

The condensation of halogen-containing compounds with aromatic hydrocarbons in the presence of catalysts of the aluminium chloride type, by the Friedel-Crafts reaction, opened a very wide field for the synthesis both of hydrocarbons and of other organic derivatives which has been extensively developed. The reaction, using chlorinated paraffins, has been utilized in the production of high-boiling viscous hydrocarbons which may be used as synthetic lubricating oils. (For a more detailed account of the Friedel-Crafts reaction, see Kranzlein [52, 1932], Groggins [25, 1930–1].)

The character of the products from the condensation of chlorinated hydrocarbons (chloroparaffins) with aromatics depends on the constitution of the initial materials, the relative proportions of chloro and aromatic components, and the reaction conditions. Low molecular weight (short chain) chloroparaffins, a high degree of chlorination, excess of aromatic component, particularly of polycyclic structure, and severe conditions of condensation lead to the production of oils of low viscosity index, high viscosity and specific gravity, of predominantly aromatic and polycyclic structure.

The use of long-chain chloroparaffins, low degree of chlorination, a smaller proportion of aromatic hydrocarbons of simple structure, and mild condensation conditions, tends to yield oils of high viscosity index, lower viscosity and specific gravity with a higher setting-point and of predominantly paraffinic structure.

It is considered that hydrocarbon oils of high molecular weight, synthesized in this manner by the Friedel-Crafts reaction, approximate more closely to petroleum lubricants in properties and constitution than the products of polymerization and olefine condensation reaction. For an account of a series of high molecular weight hydrocarbons, synthesized as ketones by the Friedel-Crafts reaction, with subsequent hydrogenation, the reader is referred to a recent paper by Mikeska [60, 1936].

Koch and Ibing [51, 1935], in discussing the production of lubricating oils by the condensation of chlorinated 'kogasin' with aromatic hydrocarbons in the presence of aluminium chloride, point out that the lubricating-oil hydrocarbons produced are of three types: Hydrocarbons formed by the condensation of two molecules of the chloroparaffin are characterized by a high hydrogen content (13·5–14·0%), a density of about 0·85, high viscosity index, and a relatively high pour-point. The oils from the condensation of one molecule of chloroparaffin with several aromatic rings have a low hydrogen content (less than 12·0%) higher density (0·9–0·95) and viscosity, with a relatively low viscosity index. By the condensation of several molecules of chloroparaffin both intramolecularly and with aromatic nuclei, hydrocarbon oils of intermediate properties are produced. The reactions involved are of a high order of complexity, intensified by cracking and polymerizing reactions induced at higher temperatures by the catalyst employed.

As stated, the Friedel-Crafts condensation has been utilized by Fischer and his collaborators [20, 1933; 21, 1934] in the synthesis of lubricants from the heavier fractions of 'kogasin' synthesized from water gas. Chlorinated derivatives of kogasin were prepared and condensed with aromatic hydrocarbons (xylene, for example) using aluminium chloride and also aluminium chloride 'sludge' as catalysts. The properties of a series of oils (residual fractions boiling above 200° C./12 mm.), refined by a bleaching-earth treatment, are briefly summarized in Table VIII.

TABLE VIII

Lubricating Oils from the Condensation of Chlorinated 'Kogasin' with Xylene

Kogasin chloro derivative	*Viscosity at 100° F., centistokes**	*Viscosity index**	*Sp. gr. 60/60° F.*
Dichloro	65	10	0·908
Trichloro	140	- 35	0·940
Tetrachloro	1,300	−100	0·981
Hexachloro	12,000	- 300	1·011

* Calculated from Fischer's data.

The viscosity and specific gravity of the product increase with increasing degree of chlorination of the initial fraction, whilst the viscosity index falls. The viscosity indices of the oils obtained are improved by decreasing the ratio of aromatic hydrocarbons to chlorokogasin; using a 1:2 proportion of xylene to a dichlorokogasin, the product had a viscosity index of 85. By hydrogenation, using a nickel catalyst, lubricants of exceptional resistance to oxidation were obtained, but with little improvement in the slope of the viscosity-temperature curve.

The synthesis of lubricating oils from the condensation of chlorinated paraffin wax with aromatic hydrocarbons in the presence of metallic aluminium as catalyst has recently been described by Hall, Wiggins, and Nash [28, 1935; 63, 1936]. The oils from trichloro-paraffin condensed with benzene, toluene, and naphthalene had uniformly high viscosity indices (of the order of 105), exceptional resistance to oxidation, and moderate pour-points (55° F.). The products obtained from monochloro-paraffin had higher viscosity indices (120) but considerably higher pour-points (85° F.). Wax-like components of high pour-point could be removed by vacuum distillation, and the residual oils then had properties analagous to those from the trichloroparaffin. The properties of typical oils prepared are summarized in the following table:

TABLE IX

Lubricating Oils from the Condensation of Chlorinated Paraffin Wax with Aromatic Hydrocarbons

Chloroparaffin used	*Mono-*	*Mono-*	*Tri-*	*Tri-*	*Tri-*
Aromatic hydrocarbon used	*toluene*	*toluene**	*benzene*	*toluene*	*naphthalene*
Viscosity at 100° F. centistokes . .	76	449	302	440	815
Viscosity index .	122	108	108	106	107
Sp. gr. 60/60° F. .	0·883	0·897	0·907	0·914	0·917
Viscosity-gravity constant . .	0·819	0·814	0·831	0·834	0·830
Pour-point, ° F. .	80	55	55	55	50
Carbon residue (Conradson), % .	0·09	0·46	0·28	0·15	1·90

* Lubricating oil = residual fraction above 300° C./3 mm.

The Friedel-Crafts synthesis is used in the production of Paraflow, a synthetic lubricating oil commercially manufactured in the United States, and used extensively for reducing the pour-point of wax-bearing lubricating-oil stocks [14, 1931]. The synthesis of such hydrocarbon oils is described in the patent [78, 1931] issued to the Standard Oil Development Company; chlorinated paraffin wax is condensed at relatively low temperatures with an aromatic hydrocarbon such as benzene or naphthalene in the presence of aluminium chloride and an inert diluent. The sludge-free product is decomposed with water and the diluent and unreacted wax removed by vacuum distillation; the characteristics and utilization of commercial 'Paraflow' oils are detailed in another article. The property of depressing the pour-point of waxy stocks has been claimed for a wide variety of products, including hydrocarbon oils prepared by condensation processes, catalytic polymerization, and by electrical treatment.

The production of lubricating oils by condensation reactions, using chlorinated hydrocarbons of varying character—ranging from chloromethanes to chlorinated petroleum and tar distillates—with aromatic hydrocarbons and aromatic-containing products, including petroleum and tar oils, has been claimed in patents by the I.G. Farbenindustrie, A.-G. [40, 1929] and others.

In synthesizing oils by the Friedel-Crafts or other reaction in which chlorinated hydrocarbons are used, traces of chloro-compounds may remain in the finished product, although minimized by effective treatment with bleaching earth. The possible deleterious effect of this residual chlorine content may be over-estimated, but it has been proposed to subject the product to the action of a reactive alkali metal to secure its complete removal [50, 1933].

Bloom-producing Agents

The green 'bloom' or fluorescence of paraffin-base petroleum lubricants (e.g. Pennsylvanian) has been attributed to the presence of high molecular weight components of complex highly condensed structure [12, 1914]. The general preference for lubricating oils of pronounced green fluorescence has led to the artificial production of 'bloom-producing agents', capable of inducing a green bloom in non-fluorescent lubricating-oil stocks. Such compounds may be obtained in a variety of condensation and polymerization reactions, and extracted by suitable means. Rial [70, 1929–32] claims their extraction from coal-tar pitches, after alkali treatment, while Harger [29, 1936] and Levin [56, 1935] obtain fluorescent agents from cracked residua after acid treatment. In their production by condensation reactions, Nash, Hunter, and Wiggins [63, 1936] extract bloom agents from the sludge after condensation of chloroparaffins with aromatics in the presence of aluminium, while Shaffer [76, 1935] proposed to condense anthracene with a sulphur dioxide extract using aluminium chloride. Birch [7, 1935] subjects polycyclic hydrocarbons, such as chrysene, to the action of aluminium chloride. The use of nitrogen-containing cyclic compounds such as aminophenyl-benzoxazole has been covered in several patents of the I.G. Farbenindustrie [42, 1933–4], who also use water- or alkali-insoluble perylene derivatives. Although dyestuffs alone rarely impart a fluorescence to an oil in which they are dissolved, Orelup [65, 1935] claims that bloom-producing agents may be prepared through treatment of dyestuffs of the acridine type with fatty acids and a water-insoluble soap.

REFERENCES

1. Allenet. B.P. 202,311 (1923); U.S.P. 1,745,028 (1930).
2. Atkinson, R. G., and Storch, H. H. *Ind. Eng. Chem.* **26**, 1120 (1934).
3. Barnard, D. P. *Nat. Petr. News*, **24** (46), 62 (1932); *J.S.A.E.* **29** (i), 40 (1931).
4. Bataaf. Petr. Maat. B.P. 441,806 (1936).
5. —— G.P. 546,516 (1931).
6. Bataaf. Petr. Maat. and Elkington. B.P. 358,068 (1931).
7. Birch, S. F. B.P. 438,425 (1935).
8. Bodroux, D. *Ann. Chim.* (x), **11**, 511 (1929).
9. B.P. 299,086 (1929), 309,199 (1927), 362,465 (1930); G.P. 516,653; F.P. 650,799; U.S.P. 1,914,727 (1929), 1,965,952 (1934).
10. B.P. 399,646 (1932); G.P. 414,237 (1934).
11. Brochet, A. *Compt. rend.* **117**, 115 (1893).
12. Brooks and Bacon. *Ind. Eng. Chem.* **6**, 623 (1914).
13. Brownlee, R. H. B.P. 141,753; U.S.P. 1,309,432; 1,374,277 (1918); cf. B.P. 414,237.
14. Davis, G. H. B., and Blackwood, A. J. *Ind. Eng. Chem.* **23**, 1452 (1931).
15. Department of Scientific and Industrial Research, Fuel Research Board Report, 1934.
16. —— Fuel Research Board Report, 1936.
17. Eichwald, E. *Z. angew. Chem.* **36**, 611 (1923); U.S.P. 1,450,026; I.G. Farbenind. A.-G. B.P. 297,798; 303,776, 305,553; 322,935.
18. Epner. B.P. 294,099; 295,705; 317,344.
19. Fischer, F. *Brenn.-Chem.* **16**, 1 (1935); c.f. Koch, H. *Brenn.-Chem.* **18**, 121 (1937).
20. Fischer, F., and Koch, H. *Brenn.-Chem.* **14**, 463 (1933).
21. Fischer, F., Koch, H., and Wiedeking, K. *Brenn.-Chem.* **15**, 229 (1934).
22. Gardner, F. T. *Ind. Eng. Chem.* **25**, 1211 (1933).
23. Gardner, H. A., and Bielouss, E. *Ind. Eng. Chem.* **14**, 619 (1922); U.S.P. 1,384,423 (1921), 1,484,018 (1924), 1,446,039 (1923); cf. B.P. 372,784–5 (1931).
24. Grignard, V., and Stratford, R. *Compt. rend.* **178**, 2149 (1924).
25. Groggins, P. H. *Ind. Eng. Chem.* **23**, 152 (1931); *Trans. Amer. Inst. Chem. Eng.* (1930).
26. Grosse, A. V., and Ipatieff, V. N. *J.A.C.S.* **57**, 2415 (1935).
27. Hall, F. C. Thesis, University of Birmingham, 1937.
28. Hall, F. C., Wiggins, W. R., and Nash, A. W. *J. Inst. Fuel*, **9** (44), 106 (1935).
29. Harger, D. K. U.S.P. 2,051,255 (1936).
30. Henderson, W. E., and Gangloff, W. C. *J.A.C.S.* **38**, 1382 (1916); **39**, 1420 (1917).
31. Hoffman, F., and Otto, M. B.P. 293,487 (1927); U.S.P. 1,811,130 (1931).
32. Hoffman, F., Otto, M., and Stegemann, W. B.P. 313,067 (1928); 307,802; U.S.P. 1,885,060; 1,933,434 (1929).

33. Howard, J. L. Thesis, University of Birmingham, 1933; cf. Hall, Wiggins, and Nash, loc. cit.
34. Howes, D. A. B.P. 363,846 (1931).
35. —— B.P. 372,763 (1932).
36. Hugel, G. *Chim. et Ind.* **26,** 1282 (1932); *Congres du Graissage,* 1931; cf. *Oel u. Kohle,* **12,** 917 (1936).
37. Hunter, W. H., and Yohe, R. V. *J.A.C.S.* **55,** 1248, 5075 (1933).
38. I.G. Farbenind. A.-G. B.P. 316,951 (1928).
39. —— B.P. 318,311, 316,701, 349,071; U.S.P. 1,850,869, 1,878,262, 1,832,629.
40. —— B.P. 320,846 (1929).
41. —— B.P. 325,832; G.P. 556,309.
42. —— B.P. 390,188 (1933); U.S.P. 1,962,564 (1934).
43. —— B.P. 345,334 (1929); U.S.P. 1,971,301.
44. —— B.P. 432,196 (1934).
45. Ipatieff, V. N. *Ber.* **44,** 2978 (1911).
46. —— *Catalytic Reactions at High Temperatures and Pressures* (Macmillan, New York, 1936).
47. Ipatieff, V. N., *et al. J.A.C.S.* **57,** 1616, 1722 (1935).
48. Ipatieff, V. N., and Grosse, A. V. *Ind. Eng. Chem.* **28,** 461 (1936).
49. Ipatieff, W., and Routala, O. *Ber.* **46,** 1748 (1913).
50. Jolly, E. M., and Swoope, C. C. U.S.P. 1,934,068 (1933).
51. Koch, K., and Ibing, G. *Brenn.-Chem.* **16,** 261 (1935).
52. Kranzlein, G. *Aluminiumchlorid in der organischen Chemie* (Verlag Chemie, Berlin, 1932).
53. Krauch, C. *Proc. Int. Conf. Bit. Coal, Pittsburgh,* **1,** 39 (1928).
54. Landa, S., and Cech, J. *Collection Czechoslav. Chem. Communication,* **5,** 204 (1933); **6,** 423 (1934).
55. Lerer, M. M. *Ann. Comb. Liq.* **8,** 681 (1933).
56. Levin, H. U.S.P. 2,024,106 (1935).
57. Lewis, W. K., and Squires, L. *Refiner,* **13,** 448 (1934).
58. Michel. B.P. 265,601 (1926), 295,990 (1927); U.S.P. 1,667,214, 1,741,472, 1,767,302; B.P. 323,100, 326,500 (1930).
59. —— G.P. 516,653 (1928); B.P. 316,274, 316,951.
60. Mikeska, L. A. *Ind. Eng. Chem.* **28,** 970 (1936).
61. Milligan, C. H., and Reid, E. E. *J.A.C.S.* **44,** 206 (1922); Berry and Reid, *J.A.C.S.* **49,** 3142 (1927).
62. Nash, A. W., Howard, J. L., and Hall, F. C. *J.I.P.T.* **20,** 1027 (1934).
63. Nash, A. W., Hunter, T. G., and Wiggins, W. R. B.P. 447,778 (1936).
64. Nash, A. W., Stanley, H. M., and Bowen, A. R. *J.I.P.T.* **16,** 830 (1930).
65. Orelup. B.P. 424,205 (1935).
66. Otto, M. *Brenn.-Chem.* **8,** 321 (1927); cf. Butlerow and Gorianov, *Ann.* **169,** 147 (1873); *Ber.* **6,** 561 (1873).
67. —— *Petr. Eng.* **2** (4), 112 (1931).
68. Otto, M., Miller, F. L., Blackwood, A. T., and Davis, G. H. B. *Refiner,* **13,** 411 (1934); cf. Terry and Parks, *Physics,* **6,** 356 (1935); Waterman, H. I., Over, J., and Tulleners A. J., *Rec. Trav. Chim.* **53,** 699 (1934).
69. Petrov, A. D., Antzuz, L. I., and Pozhiltzeva, E. N. *Refiner,* **12,** 293 (1933).
70. Rial *et al.* U.S.P.s 1,708,592 (1929), 1,839,012 (1931), 1,842,856 (1932).
71. Roegiers. 10th Congress of Industrial Chemistry, Liège (1930).
72. Rossini, F. D. *Refiner,* **14,** 266 (1935); A.P.I. Mid-Year Meeting, 1935.
73. Saint-Aunay, V. de. *Chim. et Ind.* **29,** 1011 (1933).
74. Schaarschmidt, A., and Thiele, M. *Ber.* **53,** 2128 (1920); U.S.P. 1,254,866 (1918).
75. Schildwächter, H. *Z. angew. Chem.* **47,** 677 (1934).
76. Shaffer and Fasce. U.S.P. 1,988,753 (1935).
77. Standard Oil Development Co. B.P. 432,310 (1935), 428,410, 428,438; cf. I.G. Farbenind. A.-G., B.P. 411,198, 421,118, 422,471 (1933).
78. —— U.S.P. 1,815,022 (1931); cf. I.G. Farbenind. A.-G., B.P. 415,065 (1933), 440,916 (1936).
79. Stanley, H. M. *J.S.C.I.* **49,** 349 T (1930); cf. Waterman and Tulleners, *Chim. et Ind.,* Spec. No. 496 (June 1933).
80. Sullivan, F. W., Voorhees, V., Neeley, A. W., and Shankland, R. V. *Ind. Eng. Chem.* **23,** 604 (1931); B.P. 355,214 (1930); U.S.P. 1,955,260 (1934); I.G. Farbenind. A.-G., B.P. 354,441 (1930).
81. Szayna. *Przemysl Chem.* **12,** 637 (1928).
82. Tanaka, Y., *et al. J.S.C.I. Japan,* **36,** 228 B (1933); **37,** 208 B (1934); cf. I.G. Farbenind. A.-G., B.P. 417,659 (1934).
83. Thomas, C. A., and Carmody, W. H. *Ind. Eng. Chem.* **24,** 1125 (1932).
84. Waterman, H. I., Leendertse, J. J., and de Hulster, J. *J.I.P.T.* **21,** 952 (1935); **22,** 333 (1936).
85. Wiggins, W. R. *J.I.P.T.* **22,** 305 (1936).
86. Wolf, K. *Petr. Z.* **25,** 95 (1929).
87. Woods, G. M. *Petr. Eng.* **7** (13), 158 (1936).

THE MANUFACTURE OF SYNTHETIC LUBRICATING OILS

By Dr. F. W. SULLIVAN, Jr.
Research Director, Standard Oil Company (Indiana)

It is well known that all commercial hydrocarbon lubricating oils are mixtures of many different kinds of molecules which vary in molecular weight, hydrogen:carbon ratio, and constitution. It is further recognized that even the best of the accidental mixtures to be found in nature is less desirable for lubricating purposes than some of the individual components thereof, as shown by the current decided trends towards solvent extraction of lubricating oils.

Undoubtedly the most important characteristic of lubricating oils is viscosity, and since many lubricants are used under varying conditions of temperature, it is important that viscosity vary as little as possible with temperature change. The quantitative effect of temperature changes on the viscosity of an oil, or its temperature coefficient of viscosity, depends entirely upon the nature of the hydrocarbons of which the oil is composed, and only a major change in the composition of the oil will alter it markedly in this respect. In 1929 Dean and Davis [6] proposed a useful method of indicating the viscosity-temperature susceptibility of a lubricating oil by means of a 'viscosity index' which expresses the relation of the temperature coefficient of viscosity of an oil to those of certain natural oils.

Preliminary Discussion

While the exact relationship of viscosity of lubricating oils to molecular constitution has not been definitely established, it seems fairly clear that for a given molecular weight or boiling-point the viscosities of cyclic hydrocarbons are relatively high, but change quite rapidly with temperature changes, while paraffin hydrocarbons (C_nH_{2n+2}) of the same molecular weight or boiling-point tend to be less viscous, but possess lower viscosity-temperature susceptibilities. Conversely, paraffin hydrocarbons are less volatile and possess lower specific gravities than cyclic hydrocarbons of the same viscosity, and in the case of naturally occurring oils the more highly paraffinic oils also possess higher hydrogen:carbon ratios. The high molecular weight normal paraffin hydrocarbons are solids, and the more highly paraffinic natural oils tend to have high pour-points because of the presence of these normal paraffins. The ideal lubricant would therefore appear to be one which most closely approaches the normal paraffinic structure without being solid at the lowest temperature at which the oil is to be used. Even the best of the natural paraffinic oils are far from being composed exclusively of paraffin hydrocarbons, as shown by the work of Davis and McAllister [5, 1930], which indicated that typical Pennsylvania lubricating-oil fractions contained much less hydrogen than required by the formula C_nH_{2n+2}, and probably consisted of cyclic hydrocarbons with paraffinic or isoparaffinic side-chains.

Various methods are available for synthesizing large hydrocarbon molecules with viscosities of the order of magnitude required for use as lubricating oils. Mono-olefines of the empirical composition C_nH_{2n} possess a higher hydrogen:carbon ratio than any natural mineral lubricant, and numerous investigators have shown that they can be readily polymerized by various means (notably by the action of heat, pressure, electrical discharges, or catalysts) to give viscous oils. For the production of lubricating oils, catalytic polymerization with metallic halides such as aluminium chloride or boron fluoride appears most promising. These oils, if formed by simple polymerization, would have the same hydrogen:carbon ratios as the original olefines. It appears that the polymerization of olefines with aluminium chloride at high temperature is accompanied to a certain extent by various side reactions, with the formation of some cyclic hydrocarbons. Catalytic olefine polymerization and its application to the commercial production of synthetic lubricating oils will be taken up in greater detail later. The olefines may be prepared and used as such, or the oils may be synthesized from chlorinated derivatives of saturated hydrocarbons.

Viscous oils can also be prepared by polymerization of saturated hydrocarbons, through an intermediate decomposition process. Thus conventional cracking operations are accompanied by the formation of viscous polymers which, however, are not well suited for use as lubricating oils due, among other things, to their inferior viscosity-temperature characteristics. The formation of viscous oils of this type by the action of catalysts, notably aluminium chloride, on various hydrocarbon materials has been described in numerous patents; this process is especially applicable in the case of raw materials of an aromatic nature, such as low-temperature tars. The treatment of hydrocarbon oils (or natural fatty oils), with the silent electric discharge, as exemplified by the production of 'Voltol' or 'Elektrion' oils, may also be considered to be a reaction of this general type, since this process apparently involves the elimination of hydrogen ions followed by polymerization of the resultant unsaturated residues.

The well-known Friedel-Crafts reaction affords a convenient method for synthesizing large hydrocarbon molecules, by the action of chlorinated aliphatic hydrocarbons on aromatics, in the presence of aluminium chloride, and the use of this reaction in the synthesis of lubricating oils has been described in numerous patents. The reaction is usually carried out at relatively low temperatures in order to avoid complicating side reactions such as polymerization and cracking. In this process the viscosity-temperature characteristics of the resultant oils can be controlled to a certain extent by varying the character and number of the side-chains introduced into the aromatic nucleus; thus, for example, introduction of long paraffin side-chains into an aromatic nucleus tends to produce an oil with a good viscosity index (and a relatively high pour-point). The production of lubricating oils by a very similar process, direct condensation of olefines with aromatics in the presence of a catalyst such as aluminium chloride, has also been described in numerous patents.

Hydrogenation of mineral oils, and of tars, has been used for the production of lubricating oils, the hydrogen:carbon ratio being increased thereby. However, any changes which occur in the structure of the hydrocarbons cannot be directed, and the character of the product is largely determined by the character of the starting material.

The high-boiling fractions from low-temperature carbonization tars have also been used as lubricating oils, although these oils are markedly inferior to natural petroleum oils.

As mentioned previously, catalytic polymerization of olefines with a metallic halide such as aluminium chloride or boron fluoride appears to be the most promising method of producing synthetic lubricating oils of superior quality in commerical quantities. As early as 1879 Balsohn [2] reported that ethylene and aluminium chloride reacted to form a liquid which, on treatment with water, yielded thick, oily products. Since that time numerous investigators have noted the formation of viscous oils when treating olefines with aluminium chloride or other catalysts. Thus Brownlee [4, 1919] obtained patents covering the production of lubricating oils of low specific gravity, low cold test, and high viscosity by such a process. Brownlee polymerized a cracked distillate derived from a Pennsylvania crude by agitating with aluminium chloride (2% or less, by weight) for 1 to 1½ hr. at a temperature of 300–400° F.

In 1931 F. W. Sullivan, Jr., and co-workers [12] reported the results of a comprehensive investigation of the production of synthetic lubricating oils by catalytic polymerization of olefines, carried out in the laboratories of the Standard Oil Company (Indiana) where a commercial process has been developed for the production of oils by this means. It is described in the *Ind. Eng. Chem.* cited and in U.S.P. 1,955,260 [14, 1934]. This development will be taken up in detail in the following pages.

Experimental Procedure

The apparatus used in many of the experimental polymerization runs consisted of a 6-litre cylindrical autoclave placed in a vertical position and provided with an anchor-type agitator, a thermometer well, a pressure-gauge, and plugs in the top and bottom. Other small-scale experiments were made in 4-gal. (15·1-litre) steel cylinders mounted on trunnions like a churn and provided with internal steam coils to allow heating, if desired. Semi-works experiments were conducted in a 2-bbl. (100 gal.) jacketed kettle in which agitation was accomplished by means of a centrifugal pump arranged to circulate the reaction mixture from the cone bottom to the top of the kettle. This latter design was followed in principle on the large scale and has proved quite satisfactory.

The use of polymerization temperatures as high as 300–400° F. (150–205° C.) was investigated, although most of the polymerizations were carried out at temperatures of 200° F. (93° C.) or lower, since it was found that in general lower temperatures were better from the standpoint of yield of viscous oil. Except in the case of gaseous olefines all polymerizations were carried out at low pressure—atmospheric or slightly higher. Aluminium chloride was the catalyst used in the majority of the work.

Preliminary work on the polymerization of unsaturated distillates from various sources indicated that slight variations in polymerizing conditions had but little effect on the quality of the polymerized product, but that the properties of the resultant viscous oils varied greatly when different unsaturated materials were polymerized. In order to determine the effect of the nature of the starting material on the properties of the polymerized oils several normal olefines and iso-olefines and typical representatives of cyclic unsaturated hydrocarbons were polymerized. This series included all the isomeric butenes and pentenes. Most of the olefines were prepared by dehydration of the proper alcohols over alumina. Cetene was made by the thermal decomposition of spermaceti or cetyl alcohol. In order to obviate the possibility of small differences due to variations in polymerizing conditions, a standardized procedure was adopted which is exemplified by the following illustration. A solution of 420 g. of amylene in 3 litres of naphtha, rendered inert by previous aluminium chloride treatment, was agitated with 75 g. of aluminium chloride for 8 hr. at 135° F. (57·2° C.). At the end of this time the product was allowed to settle, sludge was separated, and the supernatant solution of oil, after being washed successively with sodium hydroxide solution and water, was reduced with fire and steam to the desired viscosity. All the olefines were polymerized in naphtha solution except cetene, which was agitated with aluminium chloride at 135° F. (57·2° C.) in the absence of any diluent. An additional yield of oil could be obtained by hydrolysing the sludge, but this oil was inferior in all respects to the uncombined oil.

Experimental Results

The results of the experiments with pure olefines are given in Table I. In general it can be seen from this table that in the case of normal α-olefines the viscosity index of the polymerized oil increases in a more or less regular manner with increasing molecular weight of the raw material. This is shown graphically in Fig. 1, in which the viscosity index of the viscous oil (calculated for a viscosity of 85 sec. S.U. at 210° F.) is plotted against the number of carbon atoms in the original olefine molecule. It can be seen from Fig. 1 that the viscosity-temperature characteristics of the viscous oil produced improve very rapidly at first, with increasing length of the carbon chain in the α-olefine polymerized, and then improve more slowly in going from *n*-octene to cetene. Although the polymerized oil from cetene had a higher viscosity index than any of the other synthetic oils, it also had a high pour-point. Investigation

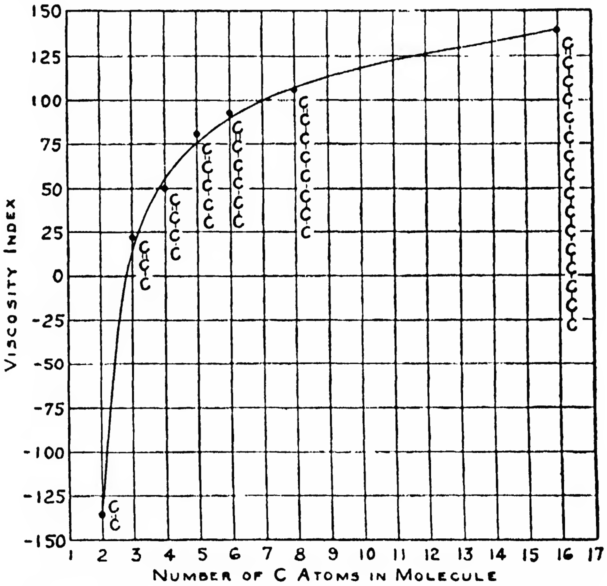


FIG. 1. Effect of saturated chain length upon the viscosity index of oils synthesized from hydrocarbons of increasing molecular weight.

showed that this high pour-point was not due to the presence of a small amount of high-melting wax, but rather that it was a natural characteristic of the entire synthetic product, which evidently had a fairly high melting-point.

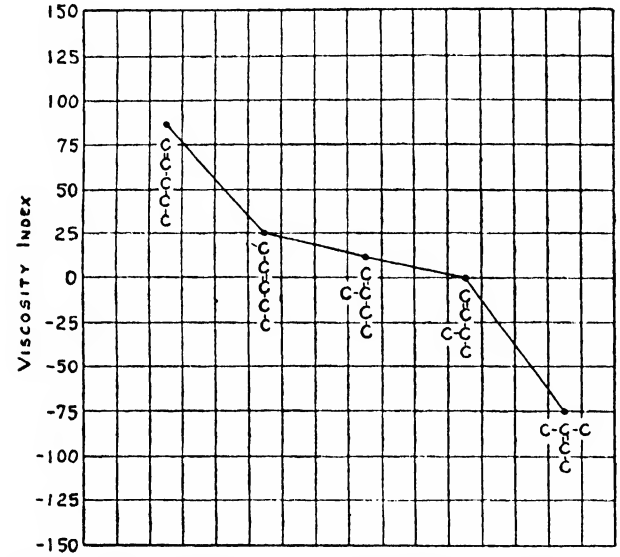


FIG. 2. Effect of interruption of the saturated chain linkage upon the viscosity index of oils synthesized from isomeric hydrocarbons.

This phenomenon apparently results only when polymerizing olefines contain very long straight chains. In the case of isomeric olefines it appears that in general the viscosity-temperature susceptibility of the polymerized oil increases with the degree of branching of the initial olefine. This tendency is illustrated in Fig. 2, which shows the variation in viscosity index obtained when the various isomeric pentenes are polymerized. Isobutylene is an exception, giving a polymerized oil with a higher viscosity index than that obtained from butene-1.

The oils obtained by polymerization of the cyclic olefines, cyclohexene and turpentine, possessed to an extreme degree the properties of naphthenic oils and, in fact, showed lower viscosity indices than any naturally occurring naphthenic oil. The oils from these cyclic olefines, as well as that from ethylene, possessed low API. gravities (high specific gravities), whereas all the other synthetic oils were characterized by approximately the same high API. gravity. These results expose in a rather striking manner the fallacy of placing too much reliance on gravity as an indication of the other characteristics of a lubricating oil. Thus it can be seen from Table I that two oils of similar viscosity may have the same API. gravity and yet have decidedly different viscosity indices.

It is interesting to note that the viscosity indices of the synthetic oils produced from the individual unsaturated hydrocarbons varied from less than −300 in the case of the oil from turpentine to +138 in the case of the oil from cetene, a far greater range than that encountered in naturally occurring oils. Fig. 3 shows the effect of temperature on the viscosity of a number of synthetic oils in comparison with naturally occurring American oils. In this chart the ratio of the Saybolt Universal viscosity at 100° F. (37·8° C.) to that at 210° F. (98·9° C.) is plotted against the viscosity at 210° F. (98·9° C.). Where more than one point is shown for the same type of synthetic oil—for example, synthetic oil from cetene—the polymerized product was reduced in several stages to progressively heavier bottoms and the viscosity-temperature characteristics of the bottoms

TABLE I

Polymerization of Pure Olefines

Olefine	*Viscosity of product**		*Yield of oil, wt. %*	*Viscosity index†*	*Grav. °API.*	*Pour test*	
	100° F. (37·8° C.), sec.	*210° F. (98·9° C.), sec.*				*° F.*	*(° C.)*
Ethylene . . .	2,769	80	..	−137	18·8	15	(−9)
Propylene . . .	1,083	70	33·3	20	33·1	−10	(−23)
Butene-1 . . .	1,654	92	..	50	34·3	−10	(−23)
	1,122	78	46·4	..	..	..	..
Butene-2 . . .	1,507	81	33·3	21	34·7	−5	(−20)
Isobutylene . .	3,706	147	42·0	67	..	..	..
	1,540	94	..	..	32·5	10	(−23)
	868	73	..	..	..	..	..
Pentene-1 . . .	1,350	94	59·8	82	..	..	..
	1,180	89	..	..	33·2	−15	(−26)
Pentene-2 . . .	1,946	93	38·5	27	32·8	0	(−18)
	976	68	53·0	..	..	..	..
3-Methylbutene-1 .	3,301	108	50·8	0	34·0	5	(−15)
	938	65	..	..	..	..	..
	321	50	..	..	..	..	..
2-Methylbutene-1 .	1,959	89	34·5	11	33·7	5	(−15)
	998	68	..	..	..	..	..
Trimethylethylene .	1,476	70	..	−74	31·0	25	(−4)
	367	49	29·3	..	..	..	..
Hexene-1 . . .	1,155	92	..	91	34·3	−25	(−32)
Octene-1 . . .	905	88	..	104	34·8	−20	(−29)
Cetene . . .	1,774	201	85	138	33·9	45	(7)
	1,187	153	..	..	34·8	45	(7)
	717	108	..	..	35·9	40	(5)
Cyclohexene . .	2,135	85	..	−27	18·0	25	(−4)
Turpentine . .	4,750	83	..	−324	15·8	30	(−1)

* The viscosity figures in all tables are Saybolt Universal viscosities.
† The viscosity index (see Dean and Davis) of each oil was calculated for a viscosity of 85 at 210° F.

were determined at each stage. It is interesting to note that the points thus determined for a synthetic oil tend to fall on a straight line, whereas the lubricating fractions from natural oils give points which fall on curves, indicating greater homogeneity of hydrocarbon type in the case of the synthetic oils. This observation is also borne out by results of experiments on extraction of the synthetic oil with selective solvents, little improvement being obtained.

The two heaviest distillate oils prepared from ethylene by Nash and his co-workers [8, 9, 1930] are also plotted in Fig. 3 for comparison. The viscosities were transposed to Saybolt and values at 100 and 210° F. (37·8 and 98·9° C.) obtained from the A.S.T.M. viscosity diagram. It is seen that these oils were distinctly inferior to natural American oils from the standpoint of viscosity-temperature characteristics, a fact that was recognized by Nash. The value for polymerized ethylene reported in Table I falls on an extension of the line through these points. For further comparison the viscosity-temperature characteristics of castor oil are also shown, using data taken from the International Critical Tables. The castor oil is seen to be somewhat better than mixed-base natural oils with respect to temperature susceptibility, although quite inferior to the natural paraffinic oils and the better synthetic oils.

Thus it appears from the foregoing that the best synthetic lube oil would be obtained by polymerization of the largest normal α-olefine that would not give solid products, since the viscosity index increases with the length of the saturated chain in the olefine polymerized and, in the absence of solid products which tend to separate out on cooling, the pour-point of an oil improves with increasing viscosity index. This generalization, that the viscosity index of the synthetic oil increases with the molecular weight of the olefine polymerized, is confirmed by results published by Fischer and co-workers in 1934 [7], who found that in the polymerization of unsaturated fractions from their synthetic 'Kogasin' with aluminium chloride the higher fractions gave the better oils. Atkinson and Storch, in 1934 [1], showed that viscous oils of markedly better viscosity index could be produced from ethylene by first polymerizing the ethylene non-catalytically to give a light, unsaturated hydrocarbon liquid and treating the latter with aluminium chloride, but even so the final oil was inferior to the better synthetic oils represented in Table I. In connexion with the polymerization of pure olefines it should also be mentioned that in 1932 Thomas and Carmody [15] reported that diolefines tend to give resinous polymers when treated with aluminium chloride, from which it appears that diolefines would be undesirable as constituents in the starting material for synthetic lubricating-oil production.

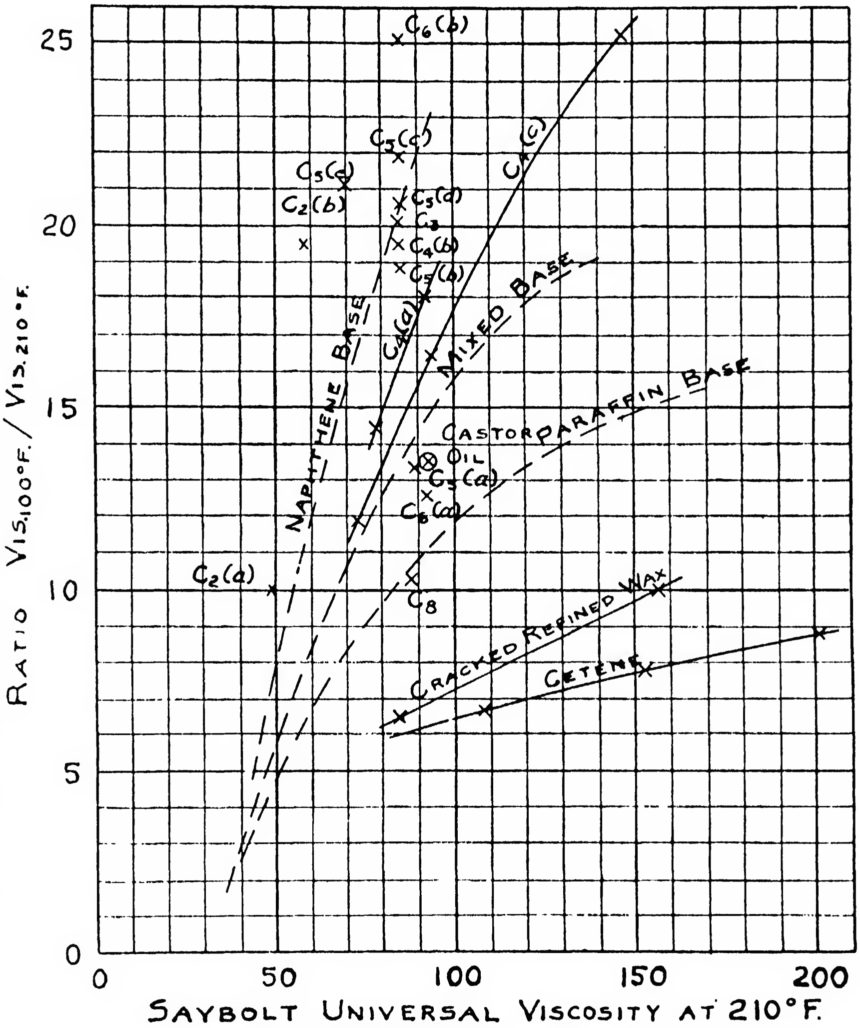


FIG. 3. Viscosity characteristics of synthetic oils.

C_2 (*a*) Ethylene (Nash).
C_2 (*b*) Ethylene (Nash).
C_3 Propylene.
C_4 (*a*) Butene-1.
C_4 (*b*) Butene-2.
C_4 (*c*) Isobutylene.
C_5 (*a*) Pentene-1.
C_5 (*b*) Pentene-2.
C_5 (*c*) 3-Methylbutene-1.
C_5 (*d*) 2-Methylbutene-1.
C_5 (*e*) Trimethylethylene.
C_6 (*a*) Hexene-1.
C_6 (*b*) Cyclohexene.
C_8 Octene-1.

The pronounced superiority of the polymers of the higher normal olefines to any natural mineral oils led to a search for an abundant source of such olefines. The cracking process immediately suggested itself as a means of obtaining unsaturated distillates for polymerization, and accordingly experiments with cracked distillates from various charging stocks were carried out. The general trends noted in the case of pure hydrocarbons were also confirmed by the results obtained with these cracked distillates as shown in Table II. These data indicate that when cracking gas-oil charging stocks to produce raw material for polymerization to viscous oil, the more paraffinic the charging stock the better is the viscosity index of the oil. In the case of wax-bearing charging stocks the higher the wax content the better is the quality of the polymerized oil. These trends are shown in a very striking manner in Table II.

Since it appeared that oils of the best quality resulted from the polymerization of normal olefines of fairly high

TABLE II

Polymerization of Cracked Distillate from Various Stocks

Stock cracked	Boiling range of distillate polymerized		Viscosity of product		Viscosity index	Yield of oil, wt. %	Pour test		Grav. ° API.
	° F.	(° C.)	100° F. (37·8° C.), sec.	210° F. (98·9° C.), sec.			° F.	(° C.)	
Winkler gas oil	225–500	(107·2–260)	3,650	86	−172	17·9	15	(−26)	15·4
Shale oil	320–420	(160–215·5)	2,430	84	−64	19·6	−15	(−26)	14·5
Wax-free Mid-Continent gas oil	300–500	(149–260)	1,500	85	41	50·5	5	(−15)	23·6
Oleic acid	Init.–300	(Init.–149)	1,420	87	52	48·0	−10	(23)	23·4
Pa. mineral seal	300–500	(149–260)	1,275	86	63	51·3	5	(−21)	26·8
Ozokerite	300–500	(149–260)	914	85	97	16·5	−35	(−37)	26·0
70% wax from sweat oil	300–500	(149–260)	835	84	103	50·0	−35	(−37)	30·8
Paraffin wax (122–40° F.)	Init.–428	(Init.–220)	797	85	109	45·0	10	(−23)	33·1
High-melting petrolatum wax (172° F.)	300–500	(149–260)	735	87	118	55·0	−35	(−37)	31·3

TABLE III

Effect of Wax Concentration on Synthetic Oil—Stock Cracked and the Distillate Polymerized

Stock cracked	Boiling range of distillate polymerized		Yield of oil, wt. %	Viscosity of product		Viscosity index*	Grav. ° API.	Pour test	
	° F.	(° C.)		100° F. (37·8° C.), sec.	210° F. (98·9° C.), sec.			° F.	(° C.)
Wax-free Mid-Continent gas oil	300–500	(149–260)	50·5	1,500	86	41	23·6	5	(−15)
40% wax	300–500	(149–260)	46·5	1,030	87	90	28·5	..	..
65% wax	Init.–530	(Init.–277)	42·2	804	77	90	29·4	−15	(−26)
70% wax	300–500	(149–260)	50·0	835	84	103	30·8	−35	(−37)
75% wax	Init.–526	(Init.–274)	44·2	840	83	99	30·9	−15	(−26)
85% wax	Init.–496	(Init.–258)	51·0	780	83	107	31·8	−20	(−29)
95% wax	Init.–590	(Init.–310)	64·1	675	86	123	34·0	−15	(−26)

* In this and subsequent tables each viscosity index was calculated directly from the viscosities given.

molecular weight, and that materials closely approximating this nature could be produced by cracking wax-bearing stocks, it remained to determine what wax content was necessary and what the permissible boiling range of the cracked distillate might be.

Samples of paraffin wax containing varying amounts of oil were cracked in the vapour phase and the unsaturated distillates were polymerized under uniform conditions. As shown in Table III, it was found that increasing amounts of oil in the wax used as charge to the cracking unit were accompanied by a regular decrease in the viscosity index of the polymerized oil obtained from the cracked distillate. The synthetic oil made by cracking refined wax and polymerizing the cracked distillate had a higher viscosity index, a higher API. gravity, and a lower pour-point than any natural lubricating oil made from known crudes. Also the yields of viscous oil were better when charging stocks containing higher percentages of wax were used. The yields in Table III are comparable, but not the maximum attainable. These results indicate that in order to be suitable for use in the production of a synthetic oil having a viscosity index of 100 or higher, the wax charged to the cracking unit should not contain more than 15% oil.

The yield of synthetic oil obtained from a cracked distillate depends on the nature of the distillate and the conditions of polymerization, while, as mentioned before, the character of the distillate determines to a large degree the quality of the polymerized oil. The major factor determining the yield of oil obtainable by polymerizing cracked distillates from paraffin wax was found to be the degree of unsaturation of the distillate, and the high yields obtained from wax are due to the unusually high degree of unsaturation of cracked distillate from this stock. The degree of unsaturation was determined by treatment of the distillate with 90% sulphuric acid, followed by a determination of the amount of polymers formed; the percentage by volume of unsaturated hydrocarbons in the original distillate was then calculated as the sum of the treating loss and the polymerization loss. As an example of the effect of the degree of unsaturation of the distillate on the yield of viscous oil, a 20% yield (by volume) of an oil having a viscosity of 200 sec. Saybolt at 210° F. (98·9° C.) was obtained by polymerization of a 60% unsaturated distillate, while polymerization of a 90% unsaturated distillate under the same conditions gave a 35% yield of 200-viscosity oil. The quality of the polymerized oil was substantially the same in both cases. The distillate used in most of the experiments described was 90% unsaturated.

In view of the pronounced differences in the viscosity indices of synthetic oils obtained by polymerizing pure, normal olefines of varying molecular weight, a sample of cracked wax distillate was fractionated into cuts of different boiling ranges and the individual fractions were polymerized separately, with the results shown in Table IV. These results confirmed the conclusions deduced from the experiments on pure olefines; namely, that the longer the straight chains in the unsaturated stock polymerized, the lower would be the viscosity-temperature susceptibility of the resulting oil. As indicated above, this general trend was also confirmed by Fischer in 1934 [7]. It can be seen from Table IV that synthetic oils with extremely high viscosity indices could be produced by polymerizing the higher boiling fractions of cracked wax distillate; for example, an oil of 85 sec. Saybolt viscosity at 210° F. (98·9° C.) with a

TABLE IV

Effect of Boiling Range of Cracked Distillate from Refined Paraffin Wax on Synthetic Oil

Distillate fraction polymerized ° *F.*	(° *C.*)	*Viscosity of product* 100° *F.* (37·8° *C.*), *sec.*	210° *F.* (98·9° *C.*) *sec.*	*Viscosity index*	*Yield of oil, wt. %*	*Grav.* ° *API.*	*Pour test* ° *F.*	(° *C.*)
Init.–200	(Init.–93·3)	1,083	83	87	52·0	31·5	–20	(–29)
200–310	(93·3–154·5)	926	85	96	52·0	31·3	–20	(–29)
310–420	(154·5–215·5)	637	84	124	69·0	34·4	–35	(–37)
420–510	(215·5–265·5)	1,565	157	123	67·5	33·7	–10	(–23)
Init.–428	(Init.–220)	797	85	109	45·0	33·1	–10	(–23)

viscosity index in the neighbourhood of 125 was produced by polymerizing a 310–510° F. (154·5–265·5° C.) fraction of the cracked distillate from refined wax. However, oils having viscosity indices of 100 or higher could be produced by polymerizing the entire cracked distillate, and on the large scale this was the stock polymerized. A distillate having an end point of about 500° F. (260° C.) was ordinarily employed, since polymerization of such a distillate gave a wax-free product while a distillate with an end point of 550 or 600° F. (288 or 315·5° C.) contained some wax, and, although the wax could be distilled from the polymerized product on reduction, to give a low pour-test bottom, a high pour-test overhead oil was obtained. It is interesting to note that in the case of cracked Mid-Continent distillates the lower-boiling fractions yielded oils with higher viscosity indices than the higher fractions, which would seem to substantiate the assumption that the naphthenic hydrocarbons were concentrated in the heavier fractions.

It was found that, in general, mixtures of unsaturated hydrocarbons gave a viscous oil the quality of which could be predicted from the properties of the oils obtained when the various components were polymerized separately. For example, the oil obtained by polymerizing a mixture of propylene and cracked paraffin wax distillate suffered the same loss in viscosity when heated from 100 to 210° F. (37·8–98·9° C.) as a blend of oils made from propylene and from cracked paraffin wax, respectively. (The relative amounts of the two oils in the latter blend were calculated, on the basis of the yields obtainable from the two starting materials, to give a blended oil containing the same proportions of propylene oil and cracked paraffin wax oil as the oil obtained by polymerizing the mixture.) Moreover, polymerization of a solution of the calculated amount of propylene in a synthetic oil from cracked paraffin wax also gave an oil with the same viscosity-temperature susceptibility as the blend just mentioned. In this connexion it should be pointed out, however, that blends of synthetic oils do not always possess the viscosity indices that might be anticipated from the viscosity-temperature characteristics of the individual components. Thus Otto and co-workers [10] announced in 1934 that synthetic oils produced by suitable polymerization of 'light ends of refinery gasoline', when blended with petroleum oils, gave products with viscosity indices far greater than would be predicted on the basis of the viscosity indices of the individual components and the blending ratios, the viscosity index of the blend being in some cases greater than that of either of the components.

In general the yield of viscous oil from cracked paraffin wax distillate was higher the lower the temperature of polymerization, provided that all the olefines were polymerized. As would be expected, longer periods of agitation were required at the lower temperatures. Although several instances have been reported in the literature, in which it was found that polymerization of olefines at higher temperatures gave increasing proportions of cyclic polymers, within the range of temperatures covered in the catalytic polymerization of cracked wax distillate (up to 300–400° F. (149–204·5° C.)), the viscosity index of the polymerized oil was not seriously affected by changes in the temperature of polymerization. The use of higher polymerization temperatures did have a pronounced effect on the nature of the aluminium chloride sludge, however; on increasing the temperature of polymerization, the sludge produced changed from a mobile liquid to a coke-like solid. The temperature finally adopted for use in large-scale polymerization was 130–5° F. (54·5–57·2° C.), and the agitation with catalyst was continued for 30 hr. at that temperature. Experimental results on the effects of time and temperature of polymerization on the yield of viscous oil from cracked paraffin wax distillate are shown in Tables V and VI, respectively.

TABLE V

Effect of Time of Polymerization on Yield of Oil

Stock, cracked distillate from 85% wax; temperature 210° F (98·9° C.).

Time, hr.	*Viscosity of product* 100° *F.* (37·8° *C.*), *sec.*	210° *F.* (98·9° *C.*), *sec.*	*Yield of oil, wt. %*	*Grav.* ° *API.*	*Pour test* ° *F.*	(° *C.*)
4	530	70	66·0	31·9	10	(–12)
4	1,791	137	36·0	30·8	–20	(–29)
9	. .	83	66·0	32·0	0	(–18)
9	. .	137	43·4	. .	. .	. .
9	2,069	154	39·0	31·0	–20	(–29)
18	623	75	68·5	31·7	. .	. .
18	2,063	152	42·0	30·8	–20	(–29)

TABLE VI

Effect of Temperature of Polymerization on Yield of Oil

Stock, cracked distillate from 85% wax.

Temp. ° *F.*	*Time, hr.*	*Viscosity of oil* 100° *F.* (37·8° *C.*), *sec.*	210° *F.* (98·9° *C.*), *sec.*	*Yield of oil, wt. %*	*Grav.* ° *API.*	*Pour test* ° *F.*	(° *C.*)
Room	114	1,273	110	51·5	30·5	5	(–15)
Room	114	2,776	155	42·5	30·5	–15	(–26)
150	18	1,172	106	56·0	31·0	–10	(–23)
150	18	2,311	158	41·0	30·3	–20	(–29)
210	18	623	75	68·5	31·7	5	(–15)
210	18	2,063	152	42·0	30·8	–20	(–29)
250	18	730	82	65·3	32·0	0	(–18)
250	18	. .	147	42·5	. .	–5	(–21)
300	18	425	63	64·5	33·4	10	(–12)
00	18	1,732	138	35·0	30·4	–10	(–23)

Although the use of lower polymerization temperatures ordinarily necessitated longer periods of agitation, the time could be shortened by the use of larger proportions of aluminium chloride. The effect of varying the proportion of catalyst is shown in Table VII. Although the use of more aluminium chloride shortened the time of polymerization at a given temperature, the amount of sludge was increased thereby, which meant a decrease in ultimate yield of available viscous oil, as well as an increase in cost of operation. As a compromise it was found desirable to use about 3% of aluminium chloride by weight, based on the cracked distillate polymerized.

TABLE VII

Effect of Aluminium Chloride Concentration on Yield of Oil

Stock, cracked distillate from 85% wax.

$AlCl_3$ *based on charge* %	*Polymerizing conditions*		*Viscosity of oil*		*Yield of oil, wt. %*	*Grav. ° API.*	*Pour test*	
	Time, hr.	*Temp. ° F.*	*100° F. (37·8° C.), sec.*	*210° F. (98·9° C.), sec.*			*° F.*	*(° C.)*
1·7	18	175–200	775	83	48·5	30·3	−10	(−23)
3·4	18	175–200	730	82	65·3	32·0	−15	(−26)
5·1	18	175–200 (79·5–93·4° C.)	765	85	60·0	31·9	−10	(−23)

It was found that the aluminium chloride sludge from a previous run could be used quite advantageously to accomplish part of the polymerization, although it was necessary to use some fresh aluminium chloride to complete the polymerization if good yields were to be obtained. For example, cracked wax distillate might be agitated for 12 hr. with the sludge from a previous run and then, after separation of the sludge, the reaction would be completed by agitation with fresh aluminium chloride for an additional 18 hr. It was also found desirable, on the large scale, to use a promoter such as carbon tetrachloride, or other chlorinated hydrocarbon, as described in U.S.P. 1,970,402 [11, 1934].

The polymerization procedure used on the large scale was essentially the same as that used in the larger experimental outfit, agitation being accomplished by means of a pump arranged to circulate the reaction mixture from the cone bottom of the polymerizer to the top. The temperature of polymerization was carefully controlled throughout the period of agitation, cooling being required during the early stages of the reaction. A polymerization plant for producing synthetic lubricating oil on the large scale is shown in Fig. 4.

After polymerization and separation of the sludge, the oil was washed with sodium hydroxide solution and then with water, reduced to the desired viscosity with fire and steam, and finally filtered through clay.

Other polymerizing agents were also tested for suitability as catalysts in the production of synthetic lubricating oils. Among the catalysts tried were silicon tetrachloride, titanium tetrachloride, stannic chloride, phosphorus pentachloride, bismuth trichloride, ferric chloride, mixtures of ferric chloride and aluminium chloride, boron fluoride and Attapulgus clay activated with hydrochloric acid. None of these substances was equal to aluminium chloride as a polymerizing agent under the conditions of temperature and pressure which were investigated, although boron fluoride proved to be a fairly active catalyst. Mixing with ferric chloride did not increase the activity of aluminium chloride as a polymerization catalyst, although instances have been reported where such mixtures were more active than either component alone in the Friedel-Crafts reaction.

Some of the properties of the synthetic oils have been mentioned before. The properties of two principal synthetic lubricating oils which are commercially available are shown in Table VIII. These two stocks have been found adequate to meet the bulk of the demands for synthetic oil —particularly as the advantages of synthetic oils over conventional lubricating oils are most pronounced in the more viscous grades. The high flash-point, high API. gravity, low change of viscosity with temperature, and excellent colour are outstanding. Since no wax is produced in the polymerization, these synthetic oils are wax-free and consequently their pour-points are in direct proportion to the viscosity-temperature susceptibilities. As the latter are low, the pour-points are also low. It is interesting to note that by the process of synthetic oil manufacture, paraffin wax —often only an undesirable by-product which has to be removed, with some difficulty, from natural paraffinic lubricating oil fractions—is converted to an oil more paraffinic than the best natural paraffinic oil, and yet entirely free from solid waxes. As a matter of interest it may be stated that the average molecular weight (determined cryoscopically) of a sample of oil 'B' in Table VIII was found to be 938.

TABLE VIII

Physical Properties of Synthetic Oils made from Paraffin Wax

	Oil A	*Oil B*
Grav., ° API.	30·6	29·7
Flash, ° F. (° C.)	515 (268)	615 (324)
Pour, ° F. (° C.)	−20 (−28·9)	0 (−17·8)
Viscosity, Saybolt Universal:		
at 100° F. (37·8° C.), sec.	850	3,250
at 210° F. (98·9° C.), sec.	85	197
Colour, N.P.A.	2	2½
Conradson carbon, %	0·13	0·4
Sligh oxidation, mg. sludge per 10 g. of oil	1·8	2·8

When heated to 100° F. (37·8° C.) with 93% sulphuric acid the synthetic oils darken and slowly evolve sulphur dioxide. At 200° F. (93·3° C.) this evolution of sulphur dioxide is quite rapid. Bromine is slowly decolorized by the synthetic oils and large quantities of hydrogen bromide are formed, indicating the presence of reactive hydrogen.

When heated to 250° F. (121·2° C.) in an open dish in an oven, the synthetic oil held its colour much better than conventional lubricating oils of the same viscosity. In general, the oxidation stability of the synthetic lubricating oils is equal, if not superior, to that of highly refined natural lubricants. Any oxidation that does occur in the case of the synthetic oils results in the formation of organic acid rather than sludge, and tests have shown the acid formation to

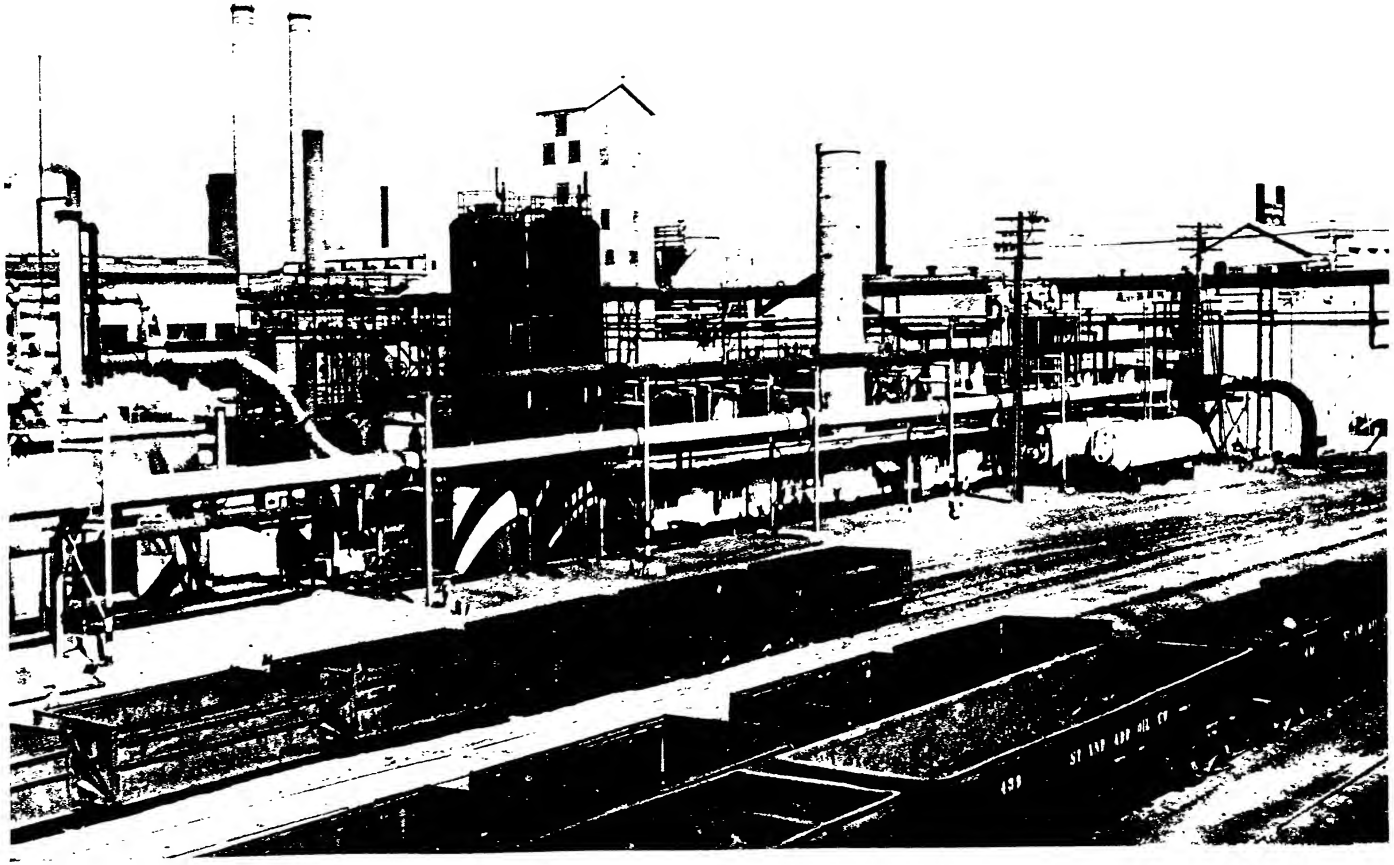


FIG. 4. Synthetic lubricating-oil plant at Whiting, Indiana. Twin polymerizers in left foreground, receivers at right with settlers and stills in background; pump-house intermediate

be of the same order of magnitude as with naturally occurring oils. The values for the Sligh oxidation test and Conradson carbon shown in Table VIII are indicative of chemical stability.

Discussion and Uses

The raw materials employed and the complicated method of manufacture make the synthetic oils inherently more expensive in the U.S.A. than conventional lubricating oils, and accordingly at the time the manufacture of the synthetic oils was started it was believed that their principal use would be in such units as transmissions, steering gears, hydraulic shock absorbers, and the like, where the amount of oil required is not large and where the practically negligible loss makes the cost of the oil of comparatively little moment. The synthetic oils are most admirably adapted to these uses, although they require blending with another stock if 'E.P.' (extreme pressure) properties are desired.

TABLE IX

Lowest Temperature at which Various Lubricants will permit satisfactory Gear-shifting

Oil	Viscosity, sec.			Viscosity index	Temperature, ° F. for 3-lb. shifting effort in transmissions no.		
	100° F.	130° F.	210° F.		1	2	3
Synthetic	3,500	1,250	200	102	18	11	11
B	5,000	1,580	200	81	34	25	25
C	12,500	2,540	200	32	57	50	50
Synthetic	2,300	930	160	106·5	11	3	3
B	3,800	1,180	160	71	29	20	20
C	8,500	1,800	160	42	52	45	45
Synthetic	1,610	640	120	100	5	−2	−2
B	2,100	770	120	78·5	18	11	11
C	4,300	1,140	120	37	42	35	35
Synthetic	800	335	80	99	−8	−16	−16
B	925	380	80	84	0	−7	−7
C	1,550	515	80	9	23	16	16
Synthetic	245	121	50	99·5	−33	−40	−40
B	285	130	50	81	−23	−29	−29
C	380	152	50	24	−7	−13	−13

The desirable viscosity characteristics of these products may be illustrated by comparison with conventional non-wax containing products as in Tables IX, X, and XI. It also appears that synthetic oils would be desirable for use in hydraulic shock absorbers and hydraulic brakes as a means of eliminating close clearances. Here, relatively high viscosities at normal temperatures could be employed without incurring excessive interference at low temperatures.

TABLE X

Permissible Temperatures of Typical Lubricants for Low-temperature Steering Effort with Cam- and Lever-type Gear

Oil	Viscosity, sec.			Temperature limit for satisfactory steering (50,000 poises), ° F.
	100° F.	130° F.	210° F.	
Synthetic	3,500	1,250	200	−25
B	5,000	1,580	200	−6
C	12,500	2,540	200	22
Synthetic	2,300	930	160	−33
B	3,800	1,180	160	−9
C	8,500	1,800	160	17

TABLE XI

Comparative Viscosities of Synthetic and Typical Oils at Normal Temperatures

Oil	Viscosity at ° F.			
	−10 Stokes*	70 sec.	100 sec.	130 sec.
Synthetic	1,300	3,250	1,100	465
A	1,300	3,000	1,050	450
B	1,300	2,400	815	335
C	1,300	1,400	465	185

* Viscosities at low temperatures are expressed as kinematic viscosities in 'stokes'; that is, the absolute viscosity in poises divided by the density of the oil.

The outstanding feature of the synthetic oils for use in the lubrication of internal-combustion engines is virtually unlimited stability towards sludge-forming oxidation, which is reflected in almost total absence of deterioration, even under strenuous engine-operating conditions. Table XII

TABLE XII

Dynamometer Tests

Test ref. group no.	Oil	Vis. at 210° F.		Acidity, mg. KOH per g.	Combustion chamber carbon, g.	Sludge, %	
		Orig.	50 hr.			Carbon	Asphaltenes
A 1	Synthetic	108	140	1·0	5·2	0·12	0·003
2	A	122	195	1·9	15·0	0·93	0·008
3	C	85	131	1·6	7·9	0·35	0·70
B 1	Synthetic	124	. .	. .	10·3	. .	0·005
2	A	123	. .	. .	12·7	. .	0·011
3	B	121	. .	. .	16·2	. .	0·045
C 1	Synthetic	75	134	. .	12·9	. .	. .
2	B	88	110	. .	16·0	. .	0·04
3	C	95	208	. .	19·3	. .	3·5
D 1	Synthetic	75	. .	. .	4·9	. .	. .
2	B	88	. .	. .	21·5	. .	. .
3	C	72	. .	. .	9·6	. .	. .

Group	Engine	r.p.m.	b.h.p.	Duration, hr.	Temperature, ° F.	
					Oil sump	Cyl. head
A	Air-cooled	1,500	24	50	275	435
B	Air-cooled	1,500	24	50	236	443
C	Air-cooled	1,500	24	50	230	430
D	Water-cooled	1,200	9	50	185	. .

gives the results of several series of dynamometer tests which serve to illustrate this particular point. The first three groups of tests in this table were conducted primarily for the purpose of obtaining comparative sludging data under rather severe conditions. The oil-sump temperatures were rather high, and in particular the cylinder temperatures indicated imposed a severe duty on the oil, as it was being continually subjected to contact with the under sides of very hot piston heads in the presence of oxygen and in a rather finely divided state. As a matter of fact these conditions were not far removed from those obtaining in air-cooled super-performance aircraft engines. All of these tests were of 50 hours' duration and were made without the addition of oil after the start of the run. This was accomplished by filling the sump at the start with 1½ times the usual amount of oil. This procedure, while not strictly in accordance with general practice, furnishes a reliable means of comparison without the necessity of compensating for 'make-up' oil in the samples. The oils used for comparison and designated 'A', 'B', and 'C' were high-grade conventional products from three different typical crude sources, covering the usual range of such sources. In every case it will be noted that the synthetic oil produced the least amount of combustion-chamber carbon, in spite of its low volatility, and that it gave the lowest asphaltene content in the crankcase oil at the end of the run. This is quite important, as it has been noted quite consistently that the more rapid the asphaltene formation, the greater the tendency towards ring-sticking. No data on asphaltene formation were obtained in the last group of tests in Table XII, as this series was carried out for the purpose of determining carbon-forming tendency only.

Conclusion

Comparison of the properties of synthetic oils with those of natural lubricating oils results in certain justifiable deductions. Natural naphthenic oils of low API. gravity and low viscosity index resemble the polymers of cyclohexene and turpentine. It therefore follows that such oils are probably polynaphthenes (or aromatics) with most of the carbon atoms in or attached to the rings. Natural paraffinic oils are of lower API. gravity for a given viscosity than the synthetic oils described, and are probably polynaphthenes in which there are relatively few rings, but in which long normal chains are prominent in the structure. These deductions are supported by consideration of the properties of the cracked distillates from such oils and of the properties of the polymers of these distillates. It is improbable that any naturally occurring lubricants are highly branched acyclic compounds.

While the major emphasis has been placed on the making of products superior to those occurring in nature, the field extending in the other direction has not been overlooked. The polymers of cyclohexene, and particularly turpentine, are more susceptible to change in viscosity with temperature than any natural oils. This is also true of the polymers of cracked distillates from naphthenic charging stocks. In general, the products obtained by the polymerization of cracked distillates from a given crude oil possess considerably poorer viscosity-temperature susceptibilities than the viscous fractions of the same crude. Further, if polymerized oils are cracked and repolymerized, the repolymerized oils become successively worse. Thus it can be seen that by proper choice of raw material synthetic oils of almost any desired properties can be produced.

REFERENCES

1. Atkinson, R. G., and Storch, H. H. *Ind. Eng. Chem.* **26**, 1120 (1934).
2. Balsohn, M. *Bull. Soc. Chim.* (2), **31**, 539 (1879).
3. Barnard, D. P. *Nat. Petr. News*, **24**, no. 46, 62 (1932).
4. Brownlee, R. H. U.S.P. 1,309,432 (8 July 1919) and 1,374,277 (12 April 1921).
5. Davis, G. H. B., and McAllister, E. N. *Ind. Eng. Chem.* **22**, 1326 (1930).
6. Dean, E. W., and Davis, G. H. B. *Chem. Met. Eng.* **36**, 618 (1929).
7. Fischer, F., Koch, H., and Wiedeking, K. *Brenn.-Chem.* **15**, 229 (1934).
8. Nash, A. W., Stanley, H. M., and Bowen, A. R. *J.I.P.T.* **16**, 830 (1930).
9. Nash, A. W., Stanley, H. M., and Bowen, A. R. *Petr. Times*, **24**, 799 (1930).
10. Otto, M., Miller, F. L., Blackwood, A. J., and Davis, G. H. B. *Oil and Gas J.* **33**, no. 26, 98 (1934).
11. Snow, H. R. U.S.P. 1,970,402 (14 Aug. 1934).
12. Sullivan, F. W., Jr., Voorhees, V., Neeley, A. W., and Shankland, R.V. *Ind. Eng. Chem.* **23**, 604 (1931); see also [13].
13. Sullivan, F. W., Jr., Voorhees, V., Oak, P. T., and Barnard, D. P. *J.S.A.E.* **29**, 40 (1931); see also [3].
14. Sullivan, F. W., Jr., and Voorhees, V. U.S.P. 1,955,260 (17 April 1934).
15. Thomas, C. A., and Carmody, W. H. *J.A.C.S.* **54**, 2480 (1932); *Ind. Eng. Chem.* **24**, 1125 (1932).

PARAFLOW

By G. H. B. DAVIS, A.B., S.M., and J. C. ZIMMER, Ph.D.
Standard Oil Development Company of New Jersey

PARAFLOW, a pure synthetic hydrocarbon oil, was introduced to the petroleum industry in the autumn of 1931 [3]. The development of Paraflow-treated lubricating oil made it possible to substitute a simple blending operation for the uneconomical dewaxing of paraffin base oils ordinarily employed to prepare lubricants which will flow freely at low temperatures. The addition of 0·25 to 1·5% of Paraflow to a wax-containing motor oil will lower the pour-point from around 30° F. to below 0° F., frequently resulting in a total reduction of 40 to 60° F. without the disadvantages incident to dewaxing to a comparable cold test.

As a result of the increasing personal and commercial dependence on all the year motor transportation under all climatic conditions, more and more pressure has been brought to bear upon the manufacturer of petroleum products for improved lubricants for low-temperature service. Prior to the development of Paraflow the only response of the petroleum industry to this demand was 'totally' dewaxed lubricants of low cold test.

The Significance of Low Cold Test

The most significant fact in connexion with low pour-point (other factors being the same) is that it has very little, if any, influence on ease of cold-weather starting or cranking speed at low temperature; but that it does facilitate the flow of oil to bearings at low temperatures which tends to prevent bearing failure and to minimize engine wear during and immediately after the motor is started.

Actual tests on motor-cars at low temperatures have been reported by Blackwood and Rickles [2, 1931] and by Larson [6, 1931] showing that cranking speed is not affected by pour-point. They report that cranking speed is a function of the extrapolated viscosity rather than the higher 'false' viscosity due to the thixotropic structure of paraffin base oils below their pour-points.

Lederer and Zublin [7, 1931] using a laboratory set-up consisting of a cylinder moving up and down at constant speed against a piston suspended from a balanced beam have obtained results which corroborate the above conclusions that hard starting does not follow the 'false' viscosity of oils below their pour-point. They feel, however, that pour-point has some bearing on cold shear or breakaway resistance.

That the cold test plays an important part in the pumping of oil to engine bearings is a well-established fact. Lederer and Zublin [7, 1931] point out that channelling at the pump with paraffin base oils occurs at about 10° F. below the pour-point. They also find that at pour temperatures or slightly above, the quantities pumped of various oils of the same viscosity at 210° F. are roughly proportional to their viscosity indices.

Becker [1, 1931] finds that extrapolated viscosities at the temperature of pumping and the pour-point of the oil are of equal importance in getting an adequate supply of oil to the bearings when starting a cold engine. Mougey [8, 1930] states that high pour oils are responsible for excessive wear in engines during cold starting due to the lubricant not reaching the rubbing surface quickly enough.

Effect of Severe Dewaxing on Lubricating Oils

Dewaxing to low pour-point has generally been thought of as giving improved lubricating oils and in many quarters dewaxed oils have been considered as of the highest quality. There remained, however, some doubt as to the soundness of this conclusion and thorough investigation has shown that with the exception of the reduced pour-point, severe dewaxing definitely lowers rather than improves the quality of lubricating oils.

The immediate effects of dewaxing upon the physical characteristics of motor oils have been studied by Davis and Blackwood [3, 1931] who found that dewaxing to 0° F. or lower pour-points resulted in decreased viscosity index and lubricating characteristics, somewhat increased volatility and poorer oxidation stability.

The decrease in the viscosity index of paraffin base oil resulting when the paraffin content is reduced becomes easily understandable when it is realized that most paraffin waxes have viscosity indices considerably higher than the best paraffin base oils from which they were obtained.

The viscosity index or temperature-viscosity relationship has been shown to be of particular significance in its effect upon cold starting, delivery of oil to bearings and oil consumption. This is apparent since for a series of given oils of the same viscosity at 210° F. the higher viscosity index oils will have lower extrapolated viscosities at 0° F. and consequently will start easier at low temperatures. On the other hand, the high-viscosity index oils have higher viscosities at elevated temperatures, for instance 350° F., and consequently will ensure adequate lubrication, with less oil consumption in a hot engine at high speed. Probably the best study of the question of oil consumption has been presented by Mougey [9, 1931], who lists four properties of the oil as contributing to oil consumption. These are (*a*) Viscosity, (*b*) Volatility, (*c*) Cold Test, and (*d*) Carbonization or sticking of piston rings.

As a result of the need for motor oils of improved performance under cold starting conditions and low consumption at subsequent hot engine temperatures there have recently appeared on the market several motor oils having viscosity indices 20 to 30% greater than those of the usual paraffin or mixed base oils. As these improved lubricants give promise of revolutionizing automotive engineers' specifications for all-year grades of motor oil it is obviously undesirable to dewax or treat a motor oil in any way which may lower its normal viscosity index.

Although the effect of dewaxing on volatility and oxidation stability is somewhat difficult to demonstrate, Davis and Blackwood [3, 1931] have shown that dewaxing does increase the volatility of motor oil, particularly of the lighter grades, by comparing the distillation temperatures for the first 40% overhead by the Vacuum Engler distillation method.

They also studied the effect of dewaxing on the resistance to oxidation of lubricating oils. The results of their laboratory oxidation tests showed that dewaxed oils were inferior to wax-containing oils in three ways, namely: volatility loss, sludge formation, and increase in viscosity. The relationship between oxidation characteristics of motor oils and their performance in internal combustion engines is too uncertain to warrant definite claims. A number of contributing factors such as moisture and dilution in the crankcase, acidity of combustion products, the effect of metal surfaces and other factors make good correlation difficult. In general, it may be concluded that those oils most resistant to oxidation will retain their lubricating properties longer than more easily oxidized oils.

Dewaxing of motor oil in addition to reducing oxidation stability also degrades the oil from the standpoint of lubrication and oiliness. In 1918 Hardy [5] reported data pertaining to the coefficient of static friction of paraffins, indicating that the paraffin waxes were slightly superior to other hydrocarbons of equivalent molecular weight, and that certain of the paraffin waxes compared favourably with oleic and stearic acids which are sometimes used as oiliness agents in lubricating oils. The oiliness characteristics of paraffin waxes have been further discussed by Robinson [10, 1933] and by Wardner [12, 1934] who concluded that portions of the petrolatum and heavy ends of bright stocks which are removed in severe dewaxing operations are responsible to a large extent for the superior lubricity of Pennsylvania motor oils. Wardner [12, 1931] has isolated and tested these natural oiliness agents which he has designated as proto petrolatum and proto oils.

The results of tests on dynamic friction machines at the Laboratories of the Standard Oil Development Company have shown that the paraffin waxes have better frictional characteristics than the oils from which they were derived. Furthermore, tests on the General Motors pin and bushing machine, which has been extensively used to determine the load-carrying ability of lubricants, indicate that the paraffin waxes are superior to oil lubricants of the same Saybolt viscosity at 210° F. [3, 1931].

Under conditions of normal operation in internal-combustion engines the variation in frictional coefficient aside from the viscosity effect is negligible. However, under unusual situations such as reduction in lubricant supply, unusually tight-fitted bearings, or during the starting and stopping periods, it may be argued that the high oiliness of certain oils will carry over the temporary deficiency without undue wear of the engine parts. To the extent that this conclusion is sound, the extra factor of safety in a waxy oil is of value in running-in new motors and during the initial operating period in cold weather.

The foregoing discussion has shown that dewaxing an oil while improving the pour-point results in an inferior product from the standpoint of viscosity index, volatility, oxidation stability, and oiliness as compared to the un-dewaxed oil of the same viscosity. Individually, the changes in most of these items are small, but collectively they are of considerable importance when producing oils of the highest quality. As a consequence, petroleum refiners have for some time devoted considerable research toward development of some means for overcoming the high pour-point of waxy oils without the disadvantages incident to severe dewaxing. Paraflow was the result of such an investigation and its development has made it possible to produce improved low-pour paraffin-base motor oils at a cost less than the equivalent dewaxing and in addition eliminated the considerable losses of material which accompany the dewaxing operation.

The Development of Paraflow

It has been known for some time that certain metallic soaps, coal-tar residues, acids, &c., and even naturally occurring constituents in oils may lower the pour-point of waxy lubricants. For instance, it is frequently observed that the pour-point of steam refined Pennsylvania residuals increases from 10 to 40° F. after clay filtration indicating that the natural pour-point reducers present in this type of oil have been removed by adsorption on the clay.

The use of the above materials for the purpose of obtaining low cold-test oils, however, has not been satisfactory. The chief difficulty is that the reduction of the pour-point is not permanent. The metallic soaps such as aluminium stearate are susceptible to moisture. Consequently, although the initial inspection of the soap-oil blend may show a low pour-point, even the small quantity of condensation moisture normally present in automotive crankcases quickly causes hydrolysis of the soap and the pour-point of the lubricant reverts to its original high value. Not only is this type of material ineffective under operating conditions, but such soaps also frequently cause serious difficulty due to their emulsification tendencies. The coal-tar or similar residues have not been employed for pour-point reduction, since, besides degrading the oil, they do not form permanent solutions in most cases. Other possible pour-point inhibitors as complex esters, amides, and similar derivatives have had little commercial application either due to instability, high cost of production, or the necessity of using comparatively large quantities in order to secure a practical degree of pour-point depression.

The development of Paraflow was the result of a detailed investigation of the possibilities of preparing synthetic lubricating oils from petroleum products. As has been indicated above, it was known that certain heavy residual lubricants contain natural pour-point reducers to a greater or less degree. In order to obtain a product of greater stability and effectiveness a series of high molecular weight lubricating oils were synthesized in the laboratory, by the so-called Friedel-Crafts condensation reaction. The most effective and stable pour-point reducers were produced by reacting chlorinated paraffin wax with naphthalene or similar aromatic nuclei in the presence of the condensation catalyst, anhydrous aluminium chloride. This product, Paraflow, is a viscous hydrocarbon oil possessing predominantly paraffinic characteristics and very similar in physical properties to a highly refined bright stock. A typical inspection of Paraflow (Table I) shows the viscosity, gravity, and carbon residue of a heavy grade of Pennsylvania bright stock. The viscosity index, however, is characteristically higher than that of ordinary oils indicating a synthetic or specially refined product. Although Paraflow itself has a pour-point of about 25° F., the addition of a small quantity to finished motor oils will lower the pour-point of the blend from 20 to 50° F. without otherwise affecting the characteristics of the lubricant.

The Paraflow treating process for the production of low-pour paraffin-base lubricants consists simply of adding ¼ to 1½% of Paraflow to the oil while vigorously agitating. As is usual when blending very small quantities of material into comparatively large volumes of liquid, very thorough agitation is necessary in order to obtain a homogeneous solution. The susceptibility of lubricating oils to Paraflow is dependent on a number of factors, the kind and quantity

TABLE I

Typical Inspections of Paraflow and Paraflow Treated Oils

	Paraflow	*S.A.E. 30 motor oil*	*Same + 1% paraflow*	*S.A.E. 10 motor oil*	*Same + 1% paraflow*
Gravity, ° API. .	23·8	27·4	27·5	30·6	30·4
Say. viscosity, 100° F. . .	3,612	474	481	150	161
Say. viscosity, 210° F. . .	214	62	62·3	44·3	44·4
Viscosity index .	106	96	97	90	99
Pour-point, ° F.	25	30	−10	30	−10
Flash-point, ° F.	555	415	415	380	395
Conradson carbon . .	1·99	0·815	0·829	0·014	0·055
Colour Robinson	¼	2¼	2	11	10
Demulsibility at 130° F. . .	..	1,620	1,620	1,620	1,620
Steam emulsion no. . . .	..	30	30	30	30

of wax, type of oil, refining process, and viscosity. These conclusions have been corroborated by Suida and Pohl [11, 1933], who have investigated the action of Paraflow on oils of all types.

The Characteristics of Paraflow Treated Oils

The effect of Paraflow on lubricating oils has been studied in detail by Davis and Blackwood [3, 1931], who report that beyond lowering the pour-point, Paraflow has no effect other than that which would be expected upon the addition of the corresponding quantity of Pennsylvania bright stock to the oil in question, Table I. Paraflow being essentially a synthetic hydrocarbon lubricating oil has no deleterious effect on demulsibility or oxidation stability. Furthermore, it is unaffected by water, is completely miscible with and cannot be separated from mineral oils by the usual methods including caustic soda or sulphuric acid treatment.

During the course of the development of Paraflow an extensive laboratory and field investigation of the properties of Paraflow treated oils was made. The results of this work showed that the reduced pour-point of Paraflow treated oils was permanent during storage under various conditions and on prolonged use in internal-combustion engines. Comparison of engine condition after operation on ordinary and Paraflow treated lubricants indicated that Paraflow has no detrimental effect on motor operation.

In discussing the significance of pour-point it was pointed out that the ease of starting a motor was independent of the actual pour-point but dependent upon the extrapolated viscosity at the operating temperature. Determination of the torque required to crank the engine at various temperatures has shown this to be true for waxy, dewaxed, and Paraflow treated oils. Measurements made simultaneously with these cranking tests in order to determine the time required for the oil to start circulating in the delivery line from the pump showed that for temperatures down to about 5° F. below the pour-point the time required to establish oil flow was dependent upon the viscosity of the lubricants at that temperature. At lower temperatures the pumpability becomes a function of the pour-point. A 25° F. pour oil showed no circulation below 10 to 15° F., while the zero pour Paraflow treated or dewaxed oils flowed at −10 to −15° F.

Additional information on pumpability of motor oils has been obtained in the Laboratory of the Standard Oil Development Company with the apparatus shown in Fig. 1. The set-up consisted essentially of an 8-ft. coil of copper tubing connected to a Cadillac oil pump which was submerged in the oil under test. In the oil line were four pressure gauges and try cocks, each 2 ft. apart, and a pressure-relief valve. The pump and oil line were placed in a cooling bath, the temperature of which was held constant within ±1° F. During operation of the pump, oil was withdrawn from the reservoir and was discharged through the pet cocks into containers so that the rate of flow could be accurately determined at any temperature or speed. The results obtained with dewaxed and Paraflow treated oil are shown in Table II. An interesting result of these tests was that the dewaxed oils failed to circulate at temperatures slightly below their pour-points due to channelling. A 1-in. core of the chilled oil extending from the pump suction to the surface of the oil in the reservoir was sucked into the pump and then flow ceased.

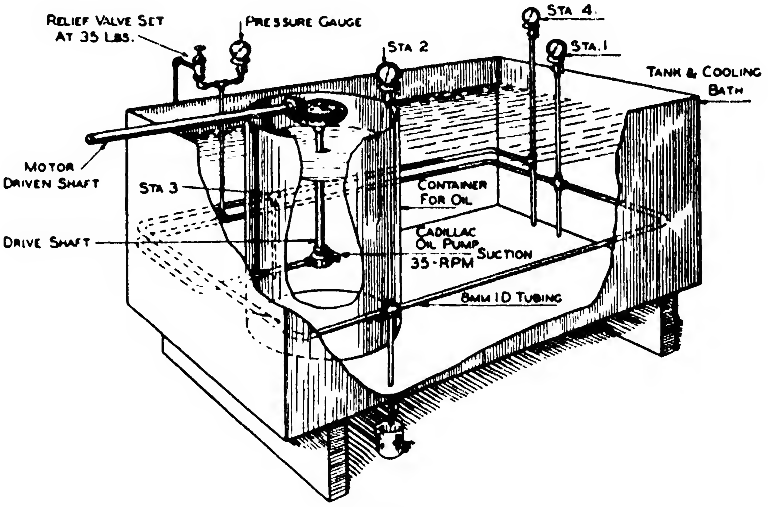


FIG. 1.

TABLE II

Cadillac Oil-pumping Tests

	Test temp. ° F.	*Time, sec.*	*Amount of oil pumped in grammes*						*Pumping rate g. per sec.*
			Relief valve	*1*	*2*	*3*	*4*	*Total*	
Dewaxed	10	183	1,657	482	1,023	..	535	3,697	20·2
Paraflow	10	198	1,430	501	1,050	184	472	3,647	18·4
Dewaxed	−10	45	307	39	76	5	*	427	9·5
Paraflow	−10	183	1,994	225	445	51	82	2,797	15·3
Dewaxed	−10	47	203	55	102	6	*	366	7·8
Paraflow	−10	187	1,918	225	446	40	52	2,701	14·5

* The dewaxed oil channelled after 45/47 sec. operation respectively and flow ceased.

It will be noted that while dewaxed oil and Paraflow treated oil have practically the same pumping rate at 10° F. (i.e. above their pour-points) the actual rate of oil circulation in the system with the Paraflow blend under test at −10° F. was nearly twice as great as the dewaxed oil even during the short period prior to complete cessation of flow of the dewaxed oil.

These pumpability tests prove that a Paraflow treated oil will circulate in a motor at temperatures below its pour-point, showing that the pour-point is not a true indication of the performance of Paraflow oil in actual service. The plasticity of these oils at low temperatures is sufficient to prevent flow at the low rates of shear encountered in the cold-test jar under the conditions of the pour test, but in larger containers or in the crankcase they will flow at considerably lower temperatures. That plasticity or viscosity is responsible for the cessation of flow is indicated by the results tabulated in Table III. Small percentages of heavy naphtha approximating the dilution found in crankcase drainings were added to Paraflow treated and ordinary waxy oils. The reduction in pour-point with viscosity is quite evident in the case of Paraflow treated oils, whereas the pour-point of the ordinary oil is not materially altered.

TABLE III

Effect of Dilution

	68/210° Motor oil without paraflow			
% dilution	*Vis./100° F.*	*Vis./210° F.*	*V.I.*	*Pour-point ° F.*
0	565	68·4	102	30
3	442	63·2	109	30
5	376	60·2	115	30
10	259	55·0	130	25
15	188	49·0	133	20

	68/210° Motor oil + 3/4 % paraflow			
% dilution	*Vis./100° F.*	*Vis./210° F.*	*V.I.*	*Pour-point ° F.*
0	571	68·4	101	5
1	521	66·8	105	0
3	450	63·6	109	−5
5	367	59·2	113	−10
10	263	54·0	125	−15
15	186	48·6	149	−30

These advantages and the reliability of the Paraflow treating process which have been evidenced by laboratory and field tests have been completely confirmed by the widespread adoption of Paraflow by the motor-oil industry. During the four-year period 1931 to 1935 more than 200 licensees who make over 1,500 brands of oil have used sufficient Paraflow to treat at least 300 million gallons of oil.

The Mechanism of Pour Depression

This wide application of Paraflow and its remarkable effect on the pour-point of paraffin base oils have naturally aroused considerable interest and speculation as to the mechanism by which only 0·5 to 1·0% of this material actually lowers the solidification temperature of a waxy oil 20–25° F.

In order to obtain an insight into the action of Paraflow it is necessary to consider the factors underlying the high pour-point of waxy oils. Ordinarily the removal of 2 to 5% of wax from a paraffin-base neutral oil will lower the pour-point some 20 to 50° F. depending upon the nature of the wax. Conversely the pour-point of a wax-free oil may be raised to the same extent by the addition of a similar amount of paraffin wax. Examination of such an oil at or below the pour temperature indicates that solidification is due to the formation of a plastic gel of wax and oil. The structure of this gel has been studied under a polarizing microscope equipped with a cold stage which could be cooled to −40° F. [13, 1933]. Wax-free oils when chilled to below their pour-point have the characteristic appearance of an amorphous solid with only occasional evidence of crystalline material when viewed with polarized light under the microscope. A Pennsylvania neutral, however, under the same conditions showed a network of interlocking elongated wax crystals (Fig. 2). High pour oils blended with bright stock, on the other hand, showed comparatively small petrolatum crystals (Fig. 3). Evidently the network of elongated wax crystals is not necessarily the only cause of the high pour-point of waxy oils, although it does play a part particularly in the overhead distillates. This was proved by running this type of oil through a homogenizer at 15 to 30° F. below the pour-point in order to break up the wax structure. This treatment resulted in an immediate reduction of some 20° F. in the solidification temperature, but on standing at this temperature recrystallization took place with a gradual increase of the pour-point to the original value. Similar attempts to lower the pour-point of cylinder stock containing small petrolatum crystals by mechanical working were unsuccessful.

Casual inspection of the oil petrolatum wax gel indicated that the oil is firmly held by the wax probably by surface adsorption and not merely entrained in wax network—although true solvation or adsorption commonly occurs only with amorphous substances such as gelatine or rubber, a limited solvation or more properly 'surface adsorption' frequently occurs between crystalline material and liquids, for example, paint pigments and their vehicles, soaps and water or oil as in lubricating greases, &c. An idea of the extent of such oil adsorption on the surface of waxy crystals can be obtained from the behaviour of paraffin and petrolatum wax-oil gels when pressed. Pressing of paraffin distillate removes the greater portion of the oil which is entrained in the free spaces between the large interlocking crystals. However, an appreciable amount of oil remains in the slack wax due to adsorption on the crystals. The oil content of petrolatum, on the other hand, cannot be reduced by pressing, partially on account of the lack of pores but also due to the increased oil adsorption which would be expected due to the greatly increased surface area of the small crystals.

These observations indicate that the high pour-point of oils containing paraffin wax are partially due to entrainment of oil in a crystal network and partially to oil adsorption on the surface of the wax, whereas the high pour-point of oils containing petrolatum wax are due almost entirely to oil adsorption on the surface of wax crystals.

The addition of Paraflow to a paraffin base-neutral oil has a marked effect on the crystallization of wax. Observation under a microscope of a waxy neutral oil containing Paraflow during chilling to and below the normal pour-point shows only a slight lowering of the crystallization or cloud temperature. However, there is a decided decrease in the size of the wax particles. Paraflow retards the growth of the crystals in proportion to its concentration up to a maximum at about 2%. Although the shape of the crystals may be changed from the needle type to small equiaxial grains, there is no evidence of any alteration in the crystal system. The extent to which crystal size may be reduced is illustrated in Figs. 4 and 5, showing photomicrographs of a 30° F. pour Pennsylvania neutral containing 0, 0·5, and 1·5% of Paraflow. The decrease in crystal size varies considerably with different oils and waxes, being necessarily only slight in the case of bright stocks

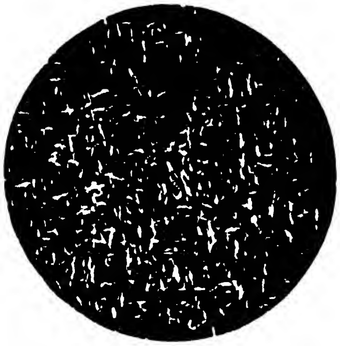


FIG. 2. 150 Pennsylvania neutral. 30 pour. 75× at 0° F.

FIG. 3. 50% bright stock. 150/210 F. 50% 150 neutral. 30 pour. 75× at 0° F.

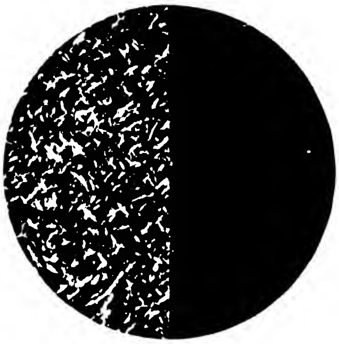


FIG. 4. 150 Pennsylvania neutral.
+0·0% Paraflow. + 1·5% Paraflow.
+30 pour. 30 pour.
75× at 0° F.

FIG. 5. 150 Pennsylvania neutral. +0·5% Paraflow. +15 pour. 75× at 0° F.

FIG. 7. 150 210 F. cyl. oil amorphous stock. + 1% special Paraflow. 100× immediately after chilling to 70 F.

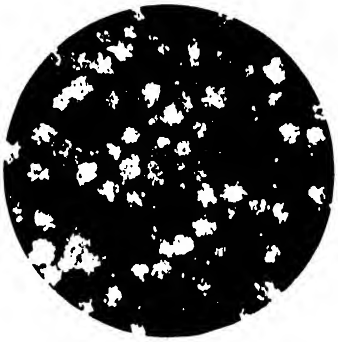


FIG. 8. 150 210° F. cyl. oil amorphous stock. + 1% special Paraflow. 100× 24 hours after chilling to 70° F.

FIG. 9. 150 neutral. + 0·5% Paraflow. 5 pour. 100× immediately after chilling to 25° F.

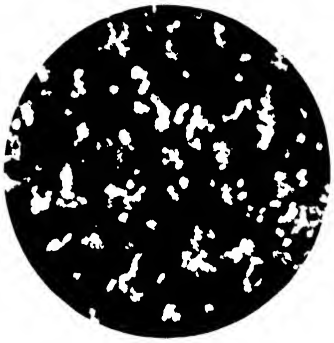


FIG. 10. 150 neutral. + 0·5% Paraflow. 5 pour. 100× 22 hours after chilling to 25° F.

FIG. 11. 150 Pennsylvania neutral. + 1·0% degras cloud inhibitor only. 30 pour. 100× 24 hours after chilling to 25° F.

or their blends which normally contain relatively small petrolatum crystals. Since these blends are susceptible to pour suppression it is apparent that the effect of Paraflow is not entirely due to reduction in the size of wax crystals.

It has been indicated above that oil adsorption probably plays the major role in causing solidification of waxy oils. Evidently, therefore, Paraflow must have some effect upon the amount of oil adsorbed by the wax. Indications of the effect of Paraflow on oil retention by wax were obtained by vacuum filtration at 32° F. of 5% wax blends in a 150 Saybolt viscosity at 100° F. wax-free synthetic oil and in a 45° API. gravity Stoddard solvent naphtha. In the presence of Paraflow there was no gel formation, and a comparatively dry wax cake containing only some 5% of oil was obtained in contrast to slushy wax mat containing some 30 to 50% of oil when no Paraflow was present.

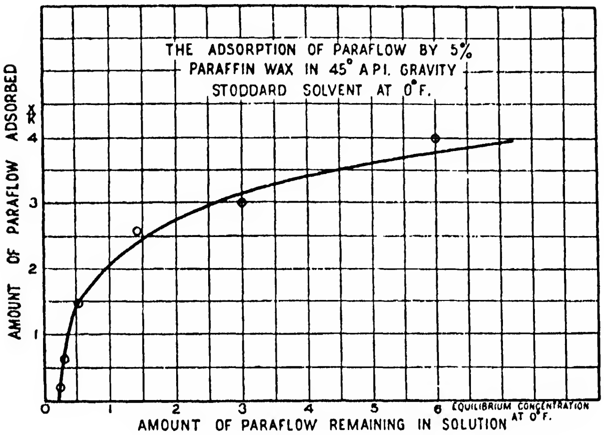


Fig. 6.

Paraflow has two effects upon wax crystallization: it reduces the size of the wax crystals and it greatly decreases the amount of oil held by the wax. The reduction in wax crystal size by Paraflow might be due either to action as a crystal-seed former or to coating over the surface of a growing wax crystal and thus stopping crystallization. It is improbable that crystal-seed formation occurs since wax-free pure Paraflow shows no indication of crystallization even at −40° F. The fact that the amount of Paraflow remaining in an oil blend after chilling and removal of the wax increases directly in relation to the quantity of Paraflow initially added indicates that coating of the crystal surface or adsorption is taking place. The distribution of Paraflow between wax and its solvent was determined by filtration at 0° F. of 5% paraffin wax blends in 45° API. gravity Stoddard solvent naphtha containing increasing amounts of Paraflow. The precipitated wax and Paraflow were blended in wax-free oil for pour determinations, and the amount of Paraflow estimated by comparison with the pour-point of similar blends containing known amounts of wax and Paraflow. The results which indicated that the distribution of Paraflow between wax and solvent follows the general adsorption laws are shown in Fig. 6. The results, although not quantitative, show that up to about 2% concentration the greater proportion of the Paraflow was removed with the wax. This value lies very near the quantity necessary to give maximum pour reduction and probably is just sufficient to coat all the wax crystals.

Further evidence of the adsorption of Paraflow on the surface of wax crystals has been found in the similarity of its action on wax and the dehydration or coagulation of colloidal dispersions by electrolytes. This effect of Paraflow on 'amorphous' and crystalline waxes is illustrated in Figs. 7 and 8. A 90-pour cylinder stock blended with 1% of a special Paraflow immediately after chilling to 70° F. and the same sample after 24 hours at this temperature, illustrates the agglomeration of the small wax particles into loose clusters. The action of Paraflow on crystalline wax in a neutral oil of 150 Saybolt viscosity at 100° F. under similar conditions is illustrated in Figs. 9 and 10. This agglomeration of wax particles is significant in that it is characteristic of all types of pour depressants so far examined. These wax clusters form only when the oil remains undisturbed and the crystals are free to move about in the fluid oil. The clusters are easily broken up by slight agitation. The effect of degras (lanoline) on a neutral oil is shown in Fig. 11. Such materials markedly reduce crystal size but do not affect the pour-point nor do they show agglomeration of wax crystals.

Thus the action of Paraflow consists essentially of coating the surface of wax crystals, thus stopping their growth and displacing the layer of adsorbed oil which ordinarily would form a high pour oil wax gel.

The deposition of Paraflow on the wax crystal and the inhibition of oil adsorption requires diffusion of the pour inhibitor through the oil layers surrounding the growing particle of wax which involves a certain time element. As a result of this slight lag in the formation of the Paraflow surface, the effect of the pour inhibitor can be partially masked by sudden shock chilling of the oil blend. If a Paraflow treated oil is chilled, say at 5 to 10° F. per min., the Paraflow does not have time to entirely inhibit oil adsorption, and the resulting shock-chilled pour-point may be 5 to 15° F. higher than would be obtained if chilling were done in the normal manner or at the much slower rate at which an automobile crankcase cools off. A similar effect may also be noted occasionally if narrow cut, very light neutral oils containing Paraflow are alternately chilled and warmed while in storage to temperatures slightly above the cloud-point without the agitation such oils receive in actual service in automobile engines. However, if small percentages of bright stocks or other heavy lubricating oil fractions are added to the light oil entirely stable low-pour blends are produced.

Paraflow as an Aid in Dewaxing Operations

The effect of Paraflow in reducing the amount of oil adsorbed or held on the surface of wax crystals and its ability to cause rapid agglomeration of small wax particles into relatively large clusters has found a wide application in the dewaxing of motor oil distillates and in the preparation of low-pour bright stocks. The presence of small quantities of Paraflow cuts down the petrolatum loss in centrifuging or cold settling of amorphous stocks and also makes it possible to cold settle the wax from heavy distillate oils which ordinarily cannot be dewaxed by cold settling.

The action of Paraflow in dewaxing by cold settling is illustrated in Tables IV and V. The data indicate more rapid settling (increased throughput) and considerably higher yield of dewaxed cylinder stock in the presence of Paraflow. The motor-oil distillate normally showed no separation of oil and wax but set to a solid gel on chilling. The addition of Paraflow prevented gelling and with the optimum amount of the dewaxing aid and rate of cooling an 80% yield of clear oil was obtained.

TABLE IV

Cold Settling Cylinder Stock in 25: 75 Solution

Chilling rate	*% paraflow*	*Volume of clear oil settled—* in 2 hr.	in 24 hr.
		%	%
100° F. to 0° F. in 2 hr.	0·0	50	66
	0·1	58	73
	0·3	63	77
	1·0	66	78
80° F. to 0° F. in 15 min.	0·0	24	60
	0·1	30	66
	0·3	32	71
	1·0	64	88

TABLE V

Effect of Paraflow in Cold Settling of Mid-Continent Motor-oil Distillates

	Amount of separation clear layer in 25:75 solution					
	0 to 30% cut		*30 to 60% cut*		*60 to 90% cut*	
% paraflow	*Untreated*	*Treated*	*Untreated*	*Treated*	*Untreated*	*Treated*
0·0	0*	0	0	0	0	0
0·25	63	16	70	15	75	2
0·5	80	55	76	36	64	3
1·0	74	69	80	58	70	43
2·0	63	80	87	58	65	55

* Solution set to a solid gel.

	Character of the Treated Distillates		
	0 to 30% cut	*20 to 60% cut*	*60 to 90% cut*
Gravity ° API. . .	28·5	28·3	28·2
Flash, ° F. . . .	430	490	540
Fire, ° F. . . .	510	575	630
Viscosity 210° F., S.U.	49·0	58·6	74·7
Colour Tag Robinson .	12	11¾	9½ +
Colour after ½ hr. at 300° F. . . .	10¼	10½	9+
Pour, ° F. . . .	105	115	130
Carbon residue, % .	..	0·21	0·50

Inasmuch as centrifuging is a mechanical means of speeding up cold settling of wax, Paraflow naturally would be expected to be equally beneficial in centrifuge dewaxing. Unfortunately, this is not always true. There are two requirements for satisfactory centrifuge operation:

(1) Easy separation of the blend into petrolatum and oil naphtha solution.

(2) Formation of petrolatum which is sufficiently fluid to prevent plugging of the bowl.

Cylinder stocks which normally can be satisfactorily centrifuged frequently form dry hard petrolatum which plugs the bowl when Paraflow is present. This is due to the fact that Paraflow greatly decreases the amount of oil held by the wax. Although this cuts down the loss of oil in the dewaxing operation, this economy does not compensate for the difficulties due to stoppage of the centrifuge bowl.

On the other hand, the addition of small amounts of Paraflow to semi-crystalline or slop wax permits a higher ratio of oil to naphtha in the blend and greatly reduces the petrolatum losses. The use of Paraflow in conjunction with small amounts of petrolatum will often permit satisfactory centrifuging of semi-crystalline cylinder stocks or slop-wax motor-oil distillates which normally cannot be satisfactorily dewaxed by this method. The economics resulting from the use of Paraflow in centrifuge dewaxing are threefold—elimination of the rerunning to partially crack slop or semi-crystalline wax cuts in order to permit centrifuge operation, increased throughput due to the higher ratio of oil to naphtha permissible, and lastly decreased losses of oil in the petrolatum fraction.

The use of Paraflow in the preparation of zero pour centrifuged motor oil also presents certain advantages. The production of 0° F. pour oils usually requires centrifuging at −50 to −60° F. As it can be conservatively estimated that refrigeration constitutes 60% of the average dewaxing cost, large economies are possible if the centrifuge dewaxing can be carried out at higher temperatures. The use of Paraflow eliminates the necessity of chilling to excessively low temperatures, and thus reduces dewaxing refrigeration costs 20 to 35%.

REFERENCES

1. Becker, A. E. *Automotive Industries*, 410 (7 March, 1931).
2. Blackwood, A. J., and Rickles, N. H. *J.S.A.E.* **29**, 236 (1931).
3. Davis, G. H. B., and Blackwood, A. J. *Ind. Eng. Chem.* **23**, 1452 (1931).
4. Davis, G. H. B. U.S.P. 1,815,022 (14 July, 1931).
5. Hardy, W. B., and Hardy, J. K. *Phil. Mag.* (6), **38**, 32 (1918).
6. Larson, C. M. Paper presented at the Amer. Soc. Mech. Engrs. Lubrication Meeting, Pennsylvania State College, 22 May, 1931.
7. Lederer, E. R., and Zublin, E. W. Paper presented at the Amer. Soc. Mech. Engrs. Lubrication Meeting, Pennsylvania State College, 22 May, 1931.
8. Mougey, H. C. Presented at the A.S.T.M. Symposium on Development of Automotive Lubricants, Detroit, Mich. 1930.
9. Mougey, H. C. *J.S.A.E.* **29**, 200 (1931).
10. Robinson, P. M. *Nat. Petr. News*, **25**, 29 (5 July, 1933).
11. Suida, H., and Pohl, H. *Petr. Z.* **29**, (23) 2, (1933).
12. Wardner, C. H. *Oil and Gas J.* **32**, (37) 12 (1934).
13. Zimmer, J. C., Davis, G. H. B., and Frolich, P. K. *Proc. of 3rd Pennsylvania Mineral Industries Conference*, Petroleum and Natural Gas Section, p. 57 (5 May, 1933).

WAXES

THE COMMERCIAL GRADES OF PARAFFIN AND THEIR APPLICATIONS

By W. J. WILSON, F.I.C., A.C.G.I., and S. T. MINCHIN, B.Sc., A.I.C.
The Burmah Oil Company, Limited

THE series of operations directed towards the preparation of paraffin in a marketable form consists of the following steps:

1. Preparation of the required wax distillate fraction.
2. Pressing of the wax distillate fraction either in single or in multiple stages; in the latter case the temperature is lowered from stage to stage of pressing. Slack wax or scale is obtained which contains from about 10% to about 30% of oil, the proportion depending on the pressing equipment and conditions.
3. Sweating of the slack wax. This has a dual objective:
   - (*a*) De-oiling of the scale to the degree required. Fully refined waxes contain less than 0·3% of oil. This operation also reduces the colour of the scale and helps, although to a limited degree, to reduce the odour.
   - (*b*) Division of the de-oiled wax into products of various setting-points, the range of which depends partly upon the paraffinic constituents existing in the slack wax, partly upon the efficiency of the sweating equipment and operation, and partly upon the methods of resweating the more oily first and middle cuts.
4. The finishing treatment for reduction of odour and colour according to market requirements.
5. Moulding and packing of the wax for distribution.

Steps 1–3 have been dealt with in other sections of this work and will be referred to in this section only in so far as they affect the quality of the finished product.

Two distinct qualities of wax are commonly produced, namely, 'Refined Paraffin' and 'White Scale'.

Refined Paraffin is, or should be, a well-sweated product containing less than 1% of oil, and more generally not more than 0·3%. It should be reasonably free from an excess of constituents of low setting-point which tend to confer excessive plasticity to the wax. It should appear quite colourless when in the solid state and only very slightly yellow in the liquid state. When the wax is to be used for impregnation or coating of paper or cartons it should be absolutely free from oily odour.

White Scale is partly refined oil-wax mixture containing generally over 2% of oil, and, due to the limited amount of sweating involved in its production, a relatively wide range of paraffin hydrocarbons, which results in the material being highly plastic. The odour and colour of white scale are often quite good.

Step No. 4 is dealt with under the heading 'Market Requirements' (see below).

The Packing of Paraffin and White Scale for Distribution

Paraffin. Refined paraffin is sold in the form of slabs. There are two main methods of slabbing, (*a*) 'Pan' moulding, (*b*) 'Press' moulding.

Pan Moulding. As the term implies, pan moulding consists of casting the paraffin in shallow pans, the dimensions of which are generally about 24×12×2½ in. The pans are charged in batteries, and the wax allowed to solidify to air temperature.

Pan-moulded wax is characterized by the relative smoothness of the surface in contact with the mould, and the rougher nature of the surface cooled by direct contact with the air.

The advantages of this method are the cheapness of the plant and the simplicity of the operation.

The disadvantages are:

- (i) The appearance of the slab so obtained is not particularly attractive, and large mottled areas are often evident.
- (ii) The crystal size tends to be comparatively large, which fact may lead to the impression that the wax is intrinsically crumbly.
- (iii) The wax, especially the grades of lower setting-point, tends to become blocked, i.e. the slabs to adhere together rather readily, when shipped under tropical conditions.
- (iv) The packing material tends to adhere to the wax.

The present trend is towards the supercession of pan moulding by press moulding.

Press Moulding. The design of press-moulding equipment varies considerably in detail, but follows the same general plan. The plant resembles a filter press, moulds and cooling plates being placed alternately on the frame and being held in position by a ram. The sides of the moulds extend above the mould proper, so that excess of liquid may remain available to fill the space caused by shrinkage during solidification. When the moulds are full of wax, cold water is circulated through the cooling plates.

The surface of press-moulded wax is dependent upon the nature of the mould surface; the wax has a semi-opaque and slightly milky appearance, and often shows a tendency to split down the vertical axis of the cake. The 'shock' cooling results in a finer crystalline structure than that of pan-moulded wax, to which it is generally superior in points (i) to (iv) enumerated above.

The disadvantages of the method are the higher cost of the plant, and the increased difficulty of preventing contamination of the wax.

The intrinsic properties of the wax are, of course, unaffected by the method of moulding employed, although this fact has not always been appreciated by consumers of wax.

By either method a slab of wax of approximately 14 lb. is usually produced.

Packing of Refined Paraffin

The slabs as described above are batched in 1 cwt. lots (8 slabs), covered with a light cotton covering, and sacked in gunny or hessian. The object of the cotton is to prevent contamination of the wax by the jute fibre of the sacking.

Method of Preparation of White Scale for Distribution

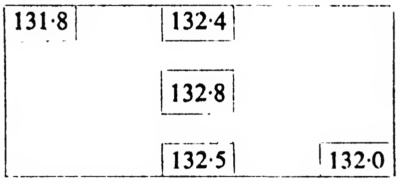
As indicated above, white scale differs from refined paraffin by its higher oil content and its greater plasticity; these characteristics, together with its lower price, account for its different method of packing and distribution.

The usual method of packing white scale is as follows. A large revolving hollow metal roller dips into the molten scale, and cooling water is passed through the roller, so that the scale solidifies in a layer. This layer is scraped off by a long knife, the edge of which is held closely against the roller, and the detached scale falls down a chute into light wooden casks.

Other Methods of Packing

The methods described above refer to the packing of most refined paraffins and scales, but they are not readily applicable to waxes of very low setting-points (about 115° F. or below). In such cases the wax may be run into 4-gallon tins, or casks, while in the molten state.

It may be noted that waxes packed in this manner, and also pan-moulded waxes, are not homogeneous solids, and the setting-point of a sample taken by coring, or broken from a slab, may not represent the true average setting-point of the whole block. The degree of variation obtainable from a pan-moulded sample is illustrated by the following diagram.



IMPORTANT PROPERTIES OF REFINED PARAFFIN FROM THE STANDPOINT OF ITS APPLICATION

General

The recognized method of classification of refined paraffin, as distinct from white scale, is by setting-point, since it is on this classification that the price is fixed.

Superficially, therefore, the only requirements to be observed by the wax producer are:

1. that the refined wax is reasonably white (a usual figure being about 0·5 Y. to 1 Y. Lovibond 18 in. cell);
2. that it is firm or plastic, according to the setting-point, and not crumbly; and
3. that the setting-point as determined by the officially recognized method is within the specified limits.

Refined paraffin, however, is remarkable for the diversity of its uses, which include candle making, impregnation or coating of wrappings and cartons, electrical uses, incorporation in polishes, and innumerable minor uses. It is to be noted that paraffin is in most cases employed on account of its peculiar physical and mechanical properties. It follows, therefore, that although the official basis of marketing is setting-point together with a reasonable degree of refinement, other properties may be of greater importance. For example, in candle making it is desirable that the wax shall form a candle which can be easily ejected from the mould; for impregnation of paper and cartons for food packing the outstanding requirement is absence of odour and taste; for electrical uses, high resistivity, high specific inductive capacity, and mechanical properties such as some degree of plasticity at low temperatures are of importance; for manufacture of polishes an essential feature is the formation of a high lustre when the wax is in association with the other ingredients employed.

It will be appreciated that these examples might be extended almost indefinitely, but sufficient has been said to make it clear that a given wax may be of the required setting-point, colour, and degree of refinement, and may yet be unsuitable for one or other of the purposes quoted.

Various properties will now be considered in detail.

Setting-point of Refined Paraffin

The method of classification by setting-point is generally the specification of the lower and upper limits of setting-point for each grade. For example, 130/135° F. grade represents paraffin having an average setting-point between these limits. The usual grades available for the market are 100/105, 106/108, 110/115, 115/118, 118/120, 122/125, 125/130, 130/135, 135/140, 140/145, 145/150. Certain grades of higher setting-point and petroleum ceresins are also produced.

The setting-point as determined is of course only an average value, the wax consisting of a number of constituents of various setting-points.

Odour and Taste

The complete absence of objectionable odour and taste in paraffin is becoming increasingly important as the application of the substance in the production of materials for packing food, tobacco, &c., becomes more general. Absence of odour is the most important property in such cases.

The evaluation of wax in this connexion is a matter of some difficulty, because odour cannot be measured quantitatively, at least so far as wax is concerned [9, 1935]. Nevertheless, it is quite possible to distinguish between odourless and nearly odourless waxes in a relatively definite manner [8, 1935]. It may be said that only comparatively few waxes reach the standard of complete absence of odour. In borderline cases the question of odour determination is liable to be a matter of mental bias on the part of the tester. In most instances, however, there is no question whether the wax is truly odourless or not.

It is obvious that the user who really requires an odourless wax cannot afford to take any risk and must err on the side of safety in all cases. At the same time, it often occurs that a wax which has been subjected to the most rigorous tests as regards odour is forthwith maltreated, e.g. by overheating, in its application by the consumer, and after a short time becomes far more odorous than any wax on the market. It can only be concluded that such maltreated waxes can in many cases be used satisfactorily for the impregnation of food wrappings, since the observance of adequate care to avoid decomposition and oxidation by its exposure to excessively high temperatures appears to be neglected with much frequency. It is therefore at first sight somewhat difficult to account for the insistence of buyers on complete absence of odour in paraffin. The probable explanation is that odours are not all equally harmful in causing contamination of foodstuffs packed in wax wrappings, and that the most objectionable odour is that of oil of kerosenic type. The presence of such kerosenic odours generally results from poor refining, and these odours are quite dissimilar to those due to decomposition or oxidation of the wax. It is probably reasonable to form a tentative conclusion that odour due to overheating is not necessarily harmful, but that odour which might be described as kerosenic is definitely detrimental. This, however, is only a general statement to which there are many exceptions, and the exercise of such precautions as will avoid the possibility of overheating of the wax is to be commended.

Foodstuffs differ in their susceptibility to odour contamination; for example, butter scotch and meat appear to be readily contaminated by being wrapped in paper waxed with malodorous wax, and in general foodstuffs containing fats appear to be sensitive to such contamination.

Odour in wax may arise from two main causes, apart from that of misuse by the consumer, to which reference has been made, and which will be discussed more fully in a later part of this article:

(i) Inadequacy or inefficiency of refining.
(ii) Contamination of the wax during the last stages of manufacture, or during shipment, storage, or distribution.

(i) **Refining.** There is no general method for the production of odourless wax at an economic cost, but the following may be mentioned as factors which require to be considered:

(*a*) *The Character of the Crude.* Waxes produced from crude oils which contain strongly odorous constituents require special care in refining.

(*b*) *The Boiling-point Range of the Press Cut.* The cut taken is naturally such that the pressing operation can be conducted at the most economic cost. In some cases the press cut may contain relatively volatile odorous constituents which contaminate the slack wax and which are removed only with difficulty in the subsequent refining operations. Distillation plant which affords good fractionation is a great aid to the production of easily refined paraffin.

(*c*) *Sweating.* As noted above, the sweating operation has a limited deodorizing effect, but the removal of odour may be substantial if the refined wax is obtained as the result of two or more sweating operations, the plant in which the final operations are conducted being kept free from odour contamination.

(*d*) *Finishing Treatment.* The finishing treatment is designed to eliminate final traces of coloured and odorous substances. It may consist of filtration through an earth such as fuller's earth or bauxite, or through bone black. If the previous stages have been conducted with efficiency, such a finishing treatment may be adequate for the production of odourless white wax.

In some cases treatment with sulphuric acid is required. In this treatment the proportions and concentration of the acid and the temperature of the treatment are all of importance, and these factors vary with waxes from different sources. This is partly because the residual oils, to which the odour may be related, are differently affected by the acid. In some cases the result of acid treatment may be a substantial reduction of the oil content, e.g. 0·5% to 0·3%, while in other cases the oil content may not be appreciably affected.

Thus each case requires to be worked out independently, and it may be taken as axiomatic that it is preferable to deal with odour elimination as early in the series of operations associated with wax production as possible, i.e. in the production of the press cut, rather than to rely on a relatively stringent finishing treatment.

(ii) **Contamination.** It is well known that paraffin is a powerful absorbent of volatile gases and odours of the organic type. It is therefore clear that after the final refinery treatment all care must be observed to avoid subsequent contamination, for example, with regard to the materials used for packing and the conditions of storage.

Colour

Closely associated with odour is colour, in the sense that any treatment which tends to produce an odourless wax also tends towards a reduction of the colour of the product. The converse, however, does not always hold good, for it is possible to apply a decolorizing treatment which has practically no deodorizing effect.

The presence of colour in finished waxes may be due to the following causes:

(*a*) To small proportions of oils, generally of a resinous or asphaltic nature.
(*b*) To 'reversion' of the wax subsequent to its refinement, i.e. development of colour in a wax which has been refined to whiteness.

With regard to (*a*) the remedy is more stringent refining.

The question of 'reversion' is a complicated one. A statement of general applicability would appear to be the somewhat obvious one that the better the refining to which the product has been subjected, the better will be its resistance to reversion. It seems probable that reversion arises from polymerization and oxidation of impurities existing in the wax, such as oil or resins. The rate and magnitude of such changes are much increased by the presence of traces of catalysts or by the action of light. Paraffin tends to hold relatively large proportions of air in contact with internal surfaces, so that if the requisite catalyst and oxidizable material are present reversion may be relatively rapid and extensive. If, however, the wax has been well refined, and substantially all impurities removed, reversion may be of negligible significance.

Oil Content of Paraffin

The oil content of wax is of considerable importance with regard to its utilization. This will be apparent from a consideration of the table shown below.

Qualitative Effect of Oil on the Structure of Waxes (S.P. 122 to 150° F.) at Normal Temperature

Oil content	*Structure*
Less than 0·3%	Hard and firm
0·3–0·5%	Slight tendency to mealiness
0·5–0·75%	Mealy to crumbly
0·75–1·25%	Crumbly to very crumbly

This classification is not to be regarded as of general application. It refers to samples of 100 to 500 g. recast by heating the wax until it was about 20° F. above the setting-point and allowing it to cool to room temperature. It is quoted simply to draw attention to the large effect of comparatively small proportions of oil upon wax structure. In this case the viscosity of the oil was 70 seconds (Redwood) at 140° F.

Waxes having setting-points below 122° F. do not exhibit this effect to anything like the same degree at normal temperatures, because the presence of constituents of very low setting-point masks the effect due to oil. However, a similar effect can be shown to exist by cooling such waxes to temperatures not less than 70° F. below their setting-points. The effect of small proportions of oil upon the structure of wax is much greater than differences which exist between waxes (of equal oil content) of different setting-points, at least within the range 122 to 150° F. For example, the structure variations at 60° F. obtained by reducing the oil content from 0·75% to nil are far greater than those existing between two waxes of 125° F. and 145° F. setting-point respectively, the latter being alike as regards oil content.

It is, of course, not necessary to use wax of low oil content for all purposes, and this fact partly explains the relatively large market for the cheaper white scale. For example, wax to be used for manufacture of candles or night-lights, or for impregnation of matches, may contain a small proportion of oil without detriment. On the other hand, waxes of low oil content are preferred for waxing paper and cartons, and in the applications of wax in the electrical industry the presence of oil is not conducive to the highest resistivity, while the crumbliness which is due to the presence of oil is definitely undesirable.

In considering the effects of the presence of oil in paraffin, it is important to note that, apart from any oil which may exist in the refined product, oil (probably liquid oxidation products) may be formed in the wax as a decomposition product if the wax be heated beyond the limits of safety as regards temperature and time. The table below gives an indication of the possible production of oil in wax due to overheating.

Increase of Oil Content due to Heating of 135/140 Paraffin in presence of Air for eight hours at Various Temperatures

Temperature of heating	*Oil content after heating*	*Oil formation due to heating*
(Fresh wax)	(0·36%)	. .
150° C.	0·39%	0·03%
200° C.	0·69%	0·33%
250° C.	1·03%	0·67%
300° C.	1·67%	1·31%
350° C.	2·65%	2·29%

The time of heating in the above example is very short in comparison with the time at which the wax is liable to be heated in industrial practice. It illustrates, however, that even relatively mild heating results in the production of oil, and stresses the necessity to maintain the operating temperature as low as possible.

The effect of oil upon structure of wax is determined by the viscosity of the oil present as well as the proportion. Since, however, the viscosities of the small proportions of oil contained in finished waxes probably differ but little, the point is not of great practical importance. Oils of low viscosity have a greater effect than those of high viscosity in promoting crumbliness.

Width of Cut

The range of paraffinic constituents present in a commercial wax is of great importance in determining the physical and mechanical properties. This characteristic is not easy to define, for the 'cut' as applied to petroleum products normally refers to range of the boiling-points of its constituents. In the utilization of paraffin, however, it is the range of setting-points that is significant, and this is not necessarily analogous to the distillation range. It can be regarded as almost certain that the paraffinic constituents in commercial waxes form solid solutions and the like so that the actual range of setting-points is not at all clearly related to the boiling-point distribution. Furthermore, it should be noted that the range of setting-points of the constituents is important only in so far as the variation of this property affects the general behaviour of the mass in a given application.

Generally, the effect of narrowing the cut is to raise the temperature at which the wax becomes plastic, as indicated by ability to be moulded between the fingers. It should be noted as a point of great significance that waxes do in fact become highly plastic at temperatures well below their setting-points, when no liquid (liquefied paraffins) is present. Two waxes of the same setting-point may exhibit large differences with regard to the temperature at which such plasticity can be observed, and the one which attains this plastic condition at the lower temperature may be regarded as being of wider cut than the other. The narrowing of the cut appears also to favour increased crystallinity of the product, but many other factors contribute to this effect.

It is interesting to note that waxes of lower setting-points attain a condition of plasticity at lower temperatures relative to the setting-point than do waxes of higher setting-points. These observations are of importance in the various applications of paraffin.

The width of cut of a finished wax is determined by the following factors:

(*a*) The width of cut of the press cut.

(*b*) The method of pressing the cut.

If the total pressable wax is obtained by pressing in one stage of cooling, the width of cut of the finished wax will tend to be wider than that of waxes obtained as the result of multiple stage filtrations and separate sweatings of the scales.

(*c*) The extent of the sweating operations. It is generally found that relatively narrow cut waxes can be obtained by the employment of several distinct sweating operations. The width of cut obtained will depend also upon the efficiency of the sweating equipment.

(*d*) The extent to which blending is effected both in the sweating process itself and in the subsequent blending which may be employed for the attainment of the required setting-points.

The width of cut can be controlled to a considerable degree, and, as might be expected from the differing methods of processing which are employed, commercial waxes show wide variations in this characteristic.

THE APPLICATIONS OF PARAFFIN

It is impossible to give a description of all the uses for which paraffin may be employed, and it will be possible to deal only with the more important utilizations. A comprehensive list of uses has, however, been compiled [1, 1934]. An excellent survey of the present methods of application and utilization has also been given by Higgs [5, 1935], and this probably represents the most up-to-date published information regarding paraffin-wax application. The discussion of this paper is also of interest.

The most important present-day application of paraffin (apart from candle manufacture) is in the proofing of materials to render them as impervious as possible to the passage of liquids (generally of an aqueous nature), water vapour, air, and occasionally fatty materials. In this category may be included the use of paraffin for insulation purposes, &c., in the electrical industries. Of special importance is the use of waxed paper and containers for the packing of foodstuffs, and, as Higgs [5, 1935] points out, the value of paraffin in this connexion 'lies in its insolubility, stability, and innocuousness. . . . The low temperature at which it can be applied ensures that the mechanical properties of the paper suffer but little damage as a result of the loss of natural moisture.'

The methods of application of the paraffin may be arranged in the following order:

(i) The formation of a continuous film over the surface of the material by dipping (surface waxing).
(ii) Penetration of the wax into the material to be proofed (impregnation).
(iii) Spraying of the liquid wax on to the surface to be proofed.

In practice method (i) gives rise to a certain amount of penetration of the wax into the material, especially if the latter is thin and relatively porous, while method (ii) usually results in the formation of a surface film as well as impregnation of the material; the degree of penetration is controlled by the time and conditions of immersion.

A factor of major importance in these processes is that of temperature. Any excessive heating of the wax, local or general, will inevitably give rise to development of odour, taste, and colour, and of increased oil content which confers crumbliness to the wax and a greater tendency for reversion of colour. It is not at all easy, however, to propose a limit of temperature, for the rate of oxidation or decomposition of wax is much affected by the presence of impurities, the surface area exposed, the efficiency of the refining to which the wax has been subjected, the setting-point, and, of course, the time at which the wax is held at an elevated temperature. It also seems likely that the most accurate qualitative representation of the mechanism of oxidation and decomposition is the assumption that the reaction takes place infinitely slowly at ordinary temperatures, the rate increasing as the temperature is raised. On this view there is no temperature which can accurately be described as 'critical' for all waxes, even if impurities are absent. The great diversity of opinion which exists is apparent from a consideration of the published work on this subject, most of which is concerned with the conversion of paraffin to fatty acids by oxidation. An excellent survey with numerous references is given by Gurwitsch [4, 1932], who concludes that the best working temperature for these oxidation processes lies between 120° and 150° C. It is clear that if substantial oxidation can occur at such relatively low temperatures, then paper waxing at such temperatures must inevitably result in a tangible amount of oxidation.

In view of these facts, it is clear that no limiting heating temperature can be indicated, especially since, as pointed out under 'Odour', the use of a wax which has been affected by heating does not always seem to be objectionable. In cases in which absence of odour and taste is imperative, the views of Scott-Harley [10, 1935] can be taken to represent the desirable conditions: 'The heating area should be as large as possible, and the heating medium should be incapable of producing a temperature exceeding 100° C. anywhere in the bath even when it is quite empty.'

In view, also, of the possible catalytic action of certain impurities in accelerating oxidation, it is advisable that the bath be thoroughly cleaned periodically, and that dust and other bodies be excluded as completely as possible.

One reason for the employment of high wax-bath temperatures would appear to be an endeavour to produce as thin a film as possible on the material waxed. It would appear, however, that this purpose is better accomplished by the adjustment of other factors, such as, for example, the heating of the material to be waxed before immersion, or decrease of the time of immersion, followed by adequate drainage of surplus wax before solidification takes place.

One example may be mentioned in which even traces of products of decomposition or oxidation may cause much trouble, namely, the manufacture of waxed-paper electrical condensers.

In this process a roll of paper and conducting strips are heated in an oven at an elevated temperature under vacuum to dry the paper thoroughly. A battery of the dehydrated rolls is placed in the empty impregnating vessel, which is filled with wax, sealed, and evacuated. The vacuum is released, the wax run out of the vessel, and the impregnated condensers removed. The wax in the plant is recycled, the loss being made up from time to time, and the plant occasionally cleaned. This brief description will serve to indicate the care which is taken in the operation to ensure complete impregnation of the wax and elimination of moisture. Even with extreme precautions it may be found that, for various causes which may be of an accidental nature, deterioration due to overheating occurs. Further, although air and moisture are eliminated from the impregnating vessels, it is probable that the film of wax on the wall of the vessel absorbs air when the condensers are removed, and that oxidation takes place to a limited degree. It may be noted that oxidation is more likely to arise from air dissolved by or absorbed in the wax film than from external air.

It is clear that the real facts relating to decomposition and oxidation of paraffin are somewhat obscure. In the past wax has been regarded as a completely inert substance, and attention has been lavished upon details of plant design and upon the material to be treated rather than upon the wax. When as much attention is given to the treatment of the wax as has been given to the rest of the equipment difficulties arising from the effects of excessive heat will be eliminated.

To impart a wax coating to the interior of a container it is sometimes thought desirable to form the coating by spraying the wax. The wax requires, of course, to be kept liquid in the spraying apparatus. If the sprays are fixed, this does not present much difficulty, but when the spraying gun is required to be movable, special heating apparatus which may be incorporated into the sprayer is necessary.

It is not clear that spraying of this type necessarily deposits liquid wax on the article undergoing waxing. The spray of molten wax cools very rapidly, and in some cases at least it would appear that the cloud is composed of solid particles. Nevertheless, it appears as if satisfactory proofing by this means is possible.

In the proofing of permeable materials it does not appear to be always essential to seal off the interstices by a film of wax over the surface. A very thin film on the walls is sufficient to render the material water repellent. It is doubtful, however, whether such waxing is of much use for stopping the diffusion of water vapour through the material. This effect of coating more or less completely the capillary walls is probably obtained when the wax is applied in the form of an emulsion.

The use of wax emulsions for various purposes appears to be growing in importance. The emulsion may be applied either by spraying or by incorporation in the material to be proofed, for example, wood pulp. It may be used also in the preparation of certain cosmetics, &c.

The formulae by which emulsions are made up are generally regarded with a certain amount of secrecy.

Emulsions may be made either with or without the use of mechanical dispersion. Soaps are the most commonly used emulsifying agents, and probably those of ethanolamine are the best. Casein has also been used with some success. Emulsions made by mechanical dispersion are usually quite stable. There does not appear to be any published information on the state of the wax in such emulsions, but it is probable that the wax exists in the solid phase at ordinary temperatures.

EMPLOYMENT OF PARAFFIN IN THE ELECTRICAL INDUSTRIES

The main applications of paraffin in the electrical industries are

1. In cable making:
   (*a*) as an ingredient (in admixture with other substances) of the insulating material;
   (*b*) as a coating of the covering for certain types of cable.
2. In electrical condenser manufacture as the dielectric medium in paper condensers.
3. In many minor uses, such as, for example, the sealing of certain types of switches, the filling of instrument transformers, the insulation of all types of windings, &c.

It is clear that in all these uses corrosion must be negligible. It will be negligible providing that the wax has not undergone oxidation. Oxidation would result also in formation of water, which is extremely undesirable in electrical uses.

Refined paraffin is valuable to the electrical industries on account of its proofing qualities and its extremely high resistivity. The resistivity of paraffin is stated to be about 5×10^{-18} ohm.-cm. at ordinary temperatures. It varies in an apparently spasmodic manner with temperature. A curve showing this effect is given by Jackson [7, 1934]. The resistivity is highest at the lowest temperature of measurement (10° C.), decreases steadily with rise of temperature to about 25° C. below the setting-point, then increases again with further rise of temperature to about 15–20° C. below the setting-point, and thereafter decreases steadily again until the setting-point is reached. This effect may be taken to be general for commercial paraffins. It seems probable that the explanation of this effect given by Jackson is not correct, and his curve should be compared with those given by Carpenter [2, 1926], referring to the coefficient of expansion of commercial paraffins at varying temperatures. The two types of curve are highly analogous, from which it may be tentatively concluded that the variations in both cases are brought about by phase changes of the paraffin in the solid state. It may be noted, however, that the change from, say, 10° C. to about 35° C. shows an approximately linear decrease of resistivity with rise of temperature. In any case, the actual change represents no serious practical loss, since even at 35° C. the conductivity is still extremely low.

The specific inductive capacity at ordinary temperatures is variously reported from 1·94 to 2·165. It would appear to decrease with refining and to rise slightly with rise of setting-point; for example, a rise of setting-point from 45° C. to 75° C. is accompanied by a rise of specific inductive capacity from 2·105 to 2·165. It is probable (unpublished work of the authors) that the specific inductive capacity shows changes with temperature somewhat analogous to those of resistivity and coefficient of expansion, falling to a minimum value at a temperature about 15–25° C. below the setting-point, and then rising again as normal temperatures are attained. It would appear that this effect is at a minimum in waxes of high setting-point over the temperature ranges likely to be encountered in use. This rule applies also to the resistivity-temperature changes.

PREPARATION OF POLISHES

The use of paraffin in polish manufacture may be ranked next in importance to its use in the paper trade (Higgs [5, 1935]). The range of polishes in which wax may be employed is very wide, including shoe polishes, wood and furniture polishes, floor and linoleum polishes, cleansing and polishing fluids [9, 1935], and others.

In general, paraffin constitutes a diluent for the more expensive waxes that are susceptible to a much higher polish than paraffin, the polishing mixture usually consisting of one or more of these higher priced waxes (e.g. beeswax, carnauba, &c.), paraffin wax, and a liquid which may be turpentine or white spirit. The paraffin enables the required consistency to be obtained without the inclusion of an excessive proportion of the more expensive materials.

An important property relative to 'paste' polishes is the ability of the paste to retain the solvent. The work of Ivanovszky [6] has shown that 'paraffin' shows poor solvent retention, but it is suggested that a good deal depends upon the type of paraffin, particularly its width of cut. It seems probable that this 'retention' may be related to the fineness of crystallization of the waxes from the solvent, fine crystallization aiding retention in increasing the relative number of intercrystal spaces, but at the same time reducing the size of these spaces. This effect will be closely related to the other waxes in the mixture, the presence of which will completely destroy the normal crystalline structure of the paraffin, so that the actual 'solvent retention' of paraffin will bear little relationship to the solvent retention of the finished polish.

THE 'DOPING' OF PARAFFIN WAX

Higgs [5, 1935] has drawn attention to the fact that the addition of high setting-point petroleum ceresin (180/185°) to paraffin has the effect of breaking down the crystallinity of the latter, with formation of a close, almost microcrystalline product even when the addition is less than 0·5%. This observation is not altogether new, since it has long been known that small proportions of added materials, such as the 'anti-mottling' agents used in candle manufacture, have a profound effect upon the crystalline structure of paraffin. The interesting feature of Higgs's statement is that the added material is of purely hydrocarbon origin, whereas anti-mottling agents are usually synthetic waxes containing acidic, esteric, or alcoholic groupings.

The suggestive implications regarding the structure of normal ceresins which arise in this connexion cannot be dealt with in this section. The practical possibilities of 'doping' are, however, considerable, since the cost of such 'doping' is not excessive, on account of the low concentrations of material required to produce the desired effect, and the modifications of the mechanical and physical properties of the wax are very marked. It is thus possible by this means to effect modification of the properties of wax to a greater extent than is possible by variation of the steps involved in its production.

The employment of a purely hydrocarbon agent has much to commend it, since it ensures that the mixture shall be non-corrosive, and that it shall retain its desirable electrical properties. Further, the agent is completely soluble in paraffin, and its effect is developed only when solution has been realized. Nevertheless, many synthetic waxes and other substances of high molecular weight which are soluble in paraffin have a similar effect, although often to a smaller degree.

The proportion of added material necessary to induce the required microcrystalline structure varies considerably according to the material used, the source of the paraffin, and the setting-point of the wax. It would appear, as a general rule, that waxes of low setting-point are more greatly affected than those of higher setting-point, and that the effect is greatest in wide cut waxes. There does not appear to be any definite relationship between the chemical composition of the agent and its effect, the essential requirements appearing to be a high molecular weight and a microcrystalline structure.

It is probable that the effect produced as regards modification of the physical and mechanical properties of the wax is not a simple function of the amount of agent added. The effect seems to be analogous to that of the addition of small proportions of metals in the production of various steels, probably a certain proportion of agent is required to produce the maximum effect, and either more or less gives an inferior result.

Details of waxing plants in present use have intentionally been omitted, because details of design and even of the methods of application are undergoing frequent changes, so that a description of such plant is liable to be out of date as soon as it is written. The object has been to discuss primarily the principles underlying the various applications which have been considered.

REFERENCES

1. Anon. *Oil, Paint and Drug Reporter*, 7 May 1934, p. 29; 14 May 1934, p. 27.
2. Carpenter, J. A. *J.I.P.T.* **12**, 288 (1926).
3. Gall, D. C. *J. Sci. Inst.* **7**, 157 (1930).
4. Gurwitsch-Moore. *Scientific Principles of Petroleum Technology*, p. 65 et seq. (Chapman and Hall, 1932).
5. Higgs, P. G. *J.I.P.T.* **21**, 1–14 (1935).
6. Ivanovszky. 'Ozokerit u. verwandte Stoffe'. A. Hartleben's Verlag. *Chemische-technische Bibliothek*, no. 397.
7. Jackson, W. *Nature*, **133**, 647 (1934).
8. Discussion in *J.I.P.T.* **21**, 18–24 (1935).
9. *J. Sci. Inst.* **12**, no. 4, 126 (1935).
10. Scott-Harley, C. R. *J.I.P.T.* **21**, 16 (1935).
11. U.S.P. 1,895,527.

CANDLES AND NIGHT-LIGHTS

By D. ALLAN, A.R.T.C., F.I.C., M.Inst.P.T.

Chief Chemist, Price's Patent Candle Company, Limited

THE use of paraffin wax in candles and night-lights did not reach any importance until about 1855 and 1857.

A brief outline of the position of the candles produced before that date will perhaps show how it came about that paraffin wax could immediately replace much of the material previously used for candle-making.

Waxes, such as beeswax and spermaceti, had been for long in use as candle materials, but they were of necessity expensive, and their use was confined to the rich and to churches. There was little machinery used for making candles of these materials, although moulding was said to have been carried out by Sieur de Brez in Paris in the fifteenth century, and the processes of pouring and rolling and of dipping were chiefly resorted to.

The wick used at the beginning of the nineteenth century was twisted cotton or linen, and snuffing was necessary. The plaiting of wick was introduced about 1820 by Cambacères, and shortly afterwards the researches of Chevreul, published in 1823, led to the manufacture of candles from fatty acids, whereas previously they had been made mainly from neutral fats. These two changes, although unconnected, are really of considerable importance to each other.

The plaited wick, while suitable for wax or spermaceti, is not suitable for tallow, as it gives much too small a consumption with the latter, resulting in guttering, but with the fatty acids it gives a consumption more in line with beeswax and spermaceti.

The subsequent development of fatty acids for candle making by hardening up by pressing led also to the development of candle-moulding machinery; for whereas the only materials which could be satisfactorily moulded had been spermaceti, and to a lesser extent beeswax, fatty acids, and particularly the solid fatty acids or stearine, lend themselves peculiarly well to moulding. The moulds were of tin or glass, and the material was air cooled in them.

In 1801 Thomas Binns of Marylebone patented a machine where steam for heating and water for cooling the moulds were introduced, for making moulded candles 'more particularly calculated for wax and spermaceti candles'. The wax at this time referred to beeswax. Various patents were taken out for candle-making machinery up to about 1855, both here and in America, and about this time the machine had developed to the prototype of the machine in use to-day.

The machinery which had been developed to deal with the manufacture of stearine candles was ready to hand with very little adjustment to deal with the new raw material, and the plaited wick was easily modified to meet the requirements of paraffin wax.

Before the development of the Scottish oil industry, the first petroleum wax recovered in any quantity was that from Rangoon crude, imported in drums and distilled in this country about 1856–7. Before this, paraffin waxes from sources other than petroleum, such as peat, had been made, but not in any quantity, and the first recorded instance of a candle made from petroleum paraffin wax was that made by James Young for Dr. Lyon, afterwards Lord Playfair. This was produced from Derbyshire oil, and it cost about 20*s.* per lb.

The paraffin wax recovered from Rangoon crude was expensive, being valued at £200 per ton, but the opening up of supplies of wax first from Scotland, then from America, put a stop to production in this country from imported crude oil, until in later years it was reintroduced by the importation in tankers from such sources as Iran, &c.

The new raw material was used mixed with stearine for several reasons. Firstly, the addition of stearine simplifies the moulding operation, the candles leaving the moulds easier and with a better surface. Secondly, wax alone, certainly at that time, would give a very fragile candle, owing to the tendency to mottle and crack. Thirdly, the addition of stearine to the wax greatly improved the stability of the candle when in a warm place, the increase in stability being quite noticeable with the addition of even 3% stearine, and increasing with the proportion and quality of the stearine. Fourthly, the addition of stearine gave opacity to the candle in proportion to its percentage. Where about 40% stearine was present, it was very similar in appearance to the pure stearine candle.

Candle Materials: Wax

The quality of paraffin wax most suitable for candle making depends on the market to be supplied. Generally speaking, waxes which do not become plastic at comparatively low temperatures are the most desirable.

Wax can be too high in melting-point as well as too low, although the latter fault, within limits, can be compensated for by the addition of stearine. Too high a melting-point wax, such as 135–140° F, used alone in a temperate climate, would give rise to complaint of difficulty in lighting, particularly in cold weather. The flame dies down to such a point that it goes out before the wax to keep it alight can be melted. The second attempt to light is even worse than the first, unless a flame is applied to the wax to melt it. It is inadvisable, therefore, to go above 130° F., and even that figure is not always safe.

As regards low melting-point material, the maximum summer temperature has to be considered, together with the nature of the wax, and whether the addition of stearine is to be made. At the same time the temperature of the candle room and cooling water must be kept in mind, as they may make moulding impossible at certain times.

Given a wax that is not too plastic, a melting-point of 120° F., preferably with 3% to 5% stearine, is the minimum that should be used to suit all seasons. If the wax tends to be plastic, the melting-point should be about 3° F. higher. The effect of 5% stearine on the stability of this type of wax is very noticeable.

Paraffin wax, since supplies of high melting-point (135–140° F.) became available, has been gradually taking the place of stearine in candles in many markets, but to a much lesser extent in Holland, France, and Belgium.

The relative merits of paraffin and stearine as candle materials depend on the purpose for which the candle is intended, and on the melting-point of the wax available. When most of the wax supplies were under 130° F. m.p., stearine was very necessary for tropical markets, but with the advent of high melting-point wax (135–140° F.) the need for large quantities of stearine diminished.

There is not a great deal of difference in luminosity between a stearine and a paraffin candle, but there is a considerable difference at the same consumption. Burning at the rate of 120 grains per hour, the light from stearine is 0·84 as compared with 1·14 from paraffin wax. Stearine candles can, however, stand a thicker wick than paraffin candles, and so the same size candle may give an equal light for a shorter period.

The main beneficial property of stearine in association with paraffin wax is the fact that it adds very greatly to its stability when subjected to undue heat, as in tropical markets. This is usually tested for by heating the candles, held horizontally at the butt, in a constant temperature bath, and noting the bend.

These tests can only be made comparatively, as absolute duplication of conditions is extremely difficult. The candles should, of course, be of the same dimensions.

It will be found that a candle made up of 80% 127° F. m.p. wax and 20% stearine 127–129° F. m.p. will give rather better stability than a candle of 136° F. m.p. made wholly of paraffin wax. The one will, of course, be semi-opaque, the other fairly transparent.

The opacity given by stearine can be imitated by the use of such materials as benzonaphthol, 0·5% of which gives an opacity about equal to that given by 35% stearine. This addition has no other beneficial properties, and it is open to objections from the manufacturing point of view. Sometimes the opacity takes several days to develop, and this leads to uncertainty as to whether the addition has been made, as it is not so easy to check its presence as it is with stearine. A further disadvantage is that the opacifier tends to come to the surface and give a kind of bloom which spoils the appearance.

The use of an opacifier with coloured candles is not to be recommended, owing to this surface development, as all blemishes on the surfaces show up usually to a greater extent when the candles are coloured.

In the absence of stearine, it is necessary to add to certain waxes something to prevent mottle. There are a number of such bodies, carnauba wax, montan wax, and lead stearate are among those commonly met with. Some waxes can be moulded satisfactorily alone, but usually conditions have to be very carefully adjusted, so that it is safer to add an anti-mottle to the extent of 0·1% or more to prevent bad work. In warm weather candles may come out of the frame free from mottle and yet develop this fault later.

Lead stearate, besides having an anti-mottling action, affects the burning of the candle, tending to straighten the wick. It also has the disadvantage that it tends to make the wick smoulder for some time after blowing out, giving an objectionable smell, and so shortening the wick as to make it difficult to relight.

Elimination of dissolved air by means of dry steam just before filling prevents mottle in some waxes, but the process has disadvantages if not very carefully supervised.

Wicks

The wick is adjusted to give proper consumption according to the diameter of the candles. The following are approximate consumptions to be aimed at with different diameters of paraffin candles; the figures are, of course, only approximate, and for wax of 123–125° F. m.p. with 3% to 5% stearine. In all cases where m.p. is used in reference to candles or waxes, the English test is referred to.

Diameter in inches .	< ½	½ to ⅝	to 11/16	to ¾	to 13/16
Consumption in grammes per hour .	4·86–5·18	6·48–7·13	7·78–8·10	8·10–8·42	8·42–8·75
Diameter in inches .	.	1	1 1/16		
Consumption in grammes per hour .	.	8·75–9·07	9·07–9·40		

The consumption will decrease with the rise in m.p. of the candles.

For special purposes, such as lamp candles, and candles for use with self-descending shades, a smaller size of wick is advisable.

In fixing the consumption of wicks for different diameters, the object aimed at is the maximum flame consistent with a good, dry, level cup and absence of smoke. These conditions, however, are not always the objective, and the maximum burning time is sometimes desired. In such cases, for instance, behaviour on relighting may be of less importance, and the size of the wick may be cut down below the figures given; but if burning conditions are not favourable, faults, such as sloppy cup and guttering, may become very bad.

The construction of the wick varies with different makers. Most of the wicks used in paraffin candles are plaited in 3 groups of yarn at so many plaits per inch. These 3 groups may contain each 5–12 or more strands of cotton, and are plaited up to 10 or 12 plaits to the inch.

In the other type, the 3 groups may each contain 3 strands twisted together, having about 5 twists per inch, and plaited from 7 to 9 plaits per inch. The yarn used in this type is coarse, 4–9s. counts, whereas the other wick may have yarn of 20–26s. counts, this finer yarn being considerably dearer.

The plaited wick is boiled with weak caustic soda, then bleached with weak hypochlorite, soured with hydrochloric acid and washed. The excess water is removed by a centrifuge and the wick treated with a solution to assist burning. These solutions vary greatly, the main ingredients being ammonium sulphate, ammonium chloride, ammonium phosphate, borax, boric acid, and potassium nitrate. The composition of the solution and the quantity has a considerable bearing on the behaviour of the wick. Phosphate is used to give rapid extinction, but too much may have the effect of producing an unduly long wick with smoky burning. After solutioning, the excess solution is removed by centrifuging, and the wicks are dried, examined, and wound on spools ready for the machines.

Manufacture of Candles

The operation of candle making is a simple one, but like many other simple processes, attention to detail is needed if candles without faults are to be produced.

The preparation of the material depends on the composition, but assuming a paraffin/stearine composition is being used, the mixture is boiled with open steam on a weak solution of sulphuric acid, and allowed to settle until bright. The settled material is run into jacket pans with steam at about 8–10 lb. in the jacket. The pan is preferably enamelled, if there is much stearine present, but aluminium is quite suitable if the proportion of stearine is not over 10%. The practice of running the candle material straight to the machines is adopted in some factories, but the method of filling from the pail gives the operator more control, and the finish of the candle is usually better.

The machines used have the moulds set in a tank, which enables them to be warmed or cooled with hot or cold water, the hot water being supplied by means of steam introduced into the water feed-pipe. The moulds are of tin, and at the ends of the rams are the tip formers, the wick being supplied up the rams through the tip, and the combination of tip and ram is used for ejecting the candles. The machine is wicked by means of a piecing stick, which is a fine wire with a hook, like a crochet needle. The wicks are drawn up and left on the bed of the machine.

In the moulding of stearine candles it is necessary to cool the stearine to about its melting-point by stirring until it is of a creamy consistency, then fill in a warm machine and cool with slightly warm water; too cold water results in cracked or otherwise damaged candles.

With paraffin and paraffin/stearine mixtures the practice is different. The candle-maker fills his pail at the jacket pan and fills the machine. After cooling, the tops are scraped off with a sharp spud or knife, and the candles are wound up into the clamps where they are held. The clamp has been adjusted so that, when the tips are lowered, the wick is held centrally for the next filling. If the first filling is clean, the machine is now ready for production. If not, it is filled until it is clean, and the waste candles go back for reboiling.

The machine being ready, the procedure will vary somewhat with the mixture being moulded, the temperature of the cooling water, and the atmospheric conditions.

The temperatures of the candle material and of the machine are adjusted, so that the material is not chilled too rapidly, which would leave marks or air holes; nor should they be too high, as this would give rise to sticking and difficulty in ejection. The operator soon acquires the necessary experience. He finds that with the return of the scrapings from the tops he can keep the material in the pan at the right temperature, and that to allow for contraction he has to fill sufficient material in the machine to give him about ½ in. on the top bed plate when cold. Experience teaches him to take the top off while it is still somewhat soft, without giving rise to hollow bottoms, due to shrinkage of the warm paraffin.

Fig. 1 shows a machine of 518 moulds being filled.

The wicks are on spools in the box below. In some cases the wicks are carried through the floor to a room below, where they are attended to by a separate operator.

Fig. 2 shows the tops being taken off with the sharp spud. The wick from these settles out when melted, as mentioned above.

Fig. 3 shows the winding up. The rams with the tip pieces, showing below the clamp at the end, force the candles from the mould, the clamp is put on and locked, when the tips are lowered ready for the next filling.

When the wax is sufficiently set and almost ready for taking off, the wicks of the candles in the clamp are cut by means of a sharp knife run along under the clamp, which is then removed, and the candles thrown on the packing bench. The tops are taken off and the candles wound up, as already described. It is essential that the tools, spud and knife, are kept very sharp, otherwise dragging of the wick and irregular wicks may arise.

Too cold water is to be avoided, as it results in cracking and bad shape. The temperature of the water should vary with the melting-point of the mixture, but this is not always possible, and care has to be taken when several qualities are being worked that one does not get cracking, &c., with high melting-point mixtures worked off the same water-supply as low melting-point. Raising the temperature of the cooling water might result in making it impossible to work the low melting-point material.

It is advisable to keep constant check on the burning of the production, as careless working may give candles with some ash, perhaps not sufficient to affect the burning seriously, but sometimes quite enough to cause the colour to go wrong.

Candles are also made by a method similar to taper making, where the wax coating is built up continuously by passing backwards and forwards through a bath of wax and dies until the required thickness is obtained. The candles are cut off to the length desired, tipped by a machine, and given a polish. This method is used in Poland. It is estimated that it would not compare favourably in cost with the previous method, and there is no comparison between the finish of the two. One advantage the Polish method has is that it makes a candle somewhat more resistant to bending than a moulded candle made from the same material.

Extrusion of candles has been suggested, but no record of a successful machine can be traced. The method of dipping or pouring and rolling used for beeswax is also to some extent used for paraffin candles for decorative purposes, but paraffin wax alone does not lend itself to this process so well as when mixed with beeswax.

The question of decorative candles has of recent years become increasingly important, and candles of almost every shape and colour are asked for. Usually the colours, which are mainly organic, are not very soluble in paraffin wax, but are reasonably soluble in stearine. The use of an opaque candle generally gives more pleasing shades than a pure paraffin-wax candle.

Self-fitting candles might be included in these decorative candles. There are two types—those with a special end moulded on the candle, and those with the end tapered down from the plain-end candles. For the former a special machine with a loose cap to form this self-fitting end is necessary, and the operation of moulding is further complicated by having to pass the wick through each cap and centre it on a bar or other support. In one type of machine these caps are fixed and each side can be removed in one lift. Shaping of self-fitting ends on plain candles is done by pressing into a hot mould or die. Tapering the ends of candles is usually carried out by means of a revolving cutter set at the necessary angle.

Unless conditions are very unfavourable, candles are usually fit to be packed immediately they are taken off the machine.

Night-lights

The manufacture of night-lights still consumes a considerable quantity of paraffin wax. They were formerly called 'Mortars' from their use in the death chamber, and were made originally of fatty matter, but at the present time most of them are made of paraffin wax.

There are three principal types of night-light.

1. Paper-cased lights for use with water.
2. Paper-cased lights for use without water.
3. Lights to burn in glass or metal containers.

Unlike a candle, the night-light is not intended to give great illumination, but to maintain a uniform light over a fairly long period. The consumption varies from 2·6 to 3·2 grammes per hour—roughly about one-third of that of a candle—the latter figure being usual when the lights are used for heating purposes, as in food-warmers. Consequently the

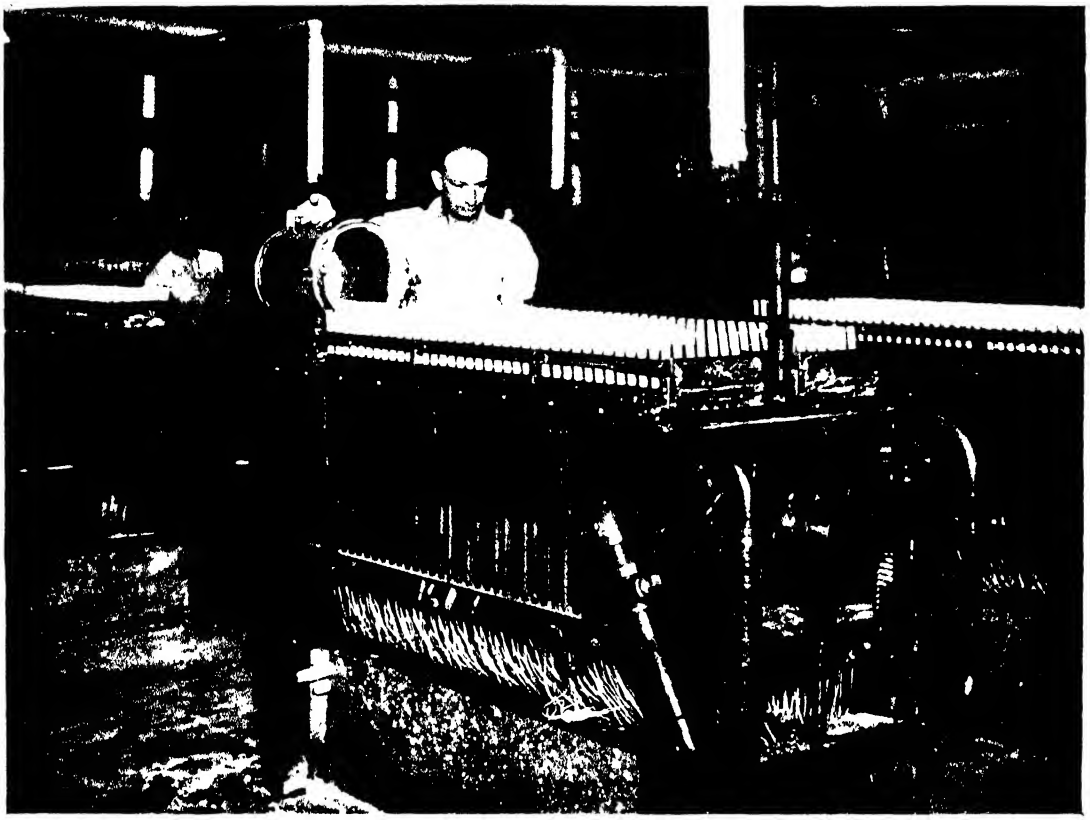


FIG. 1. Candle Making—Filling the Moulds

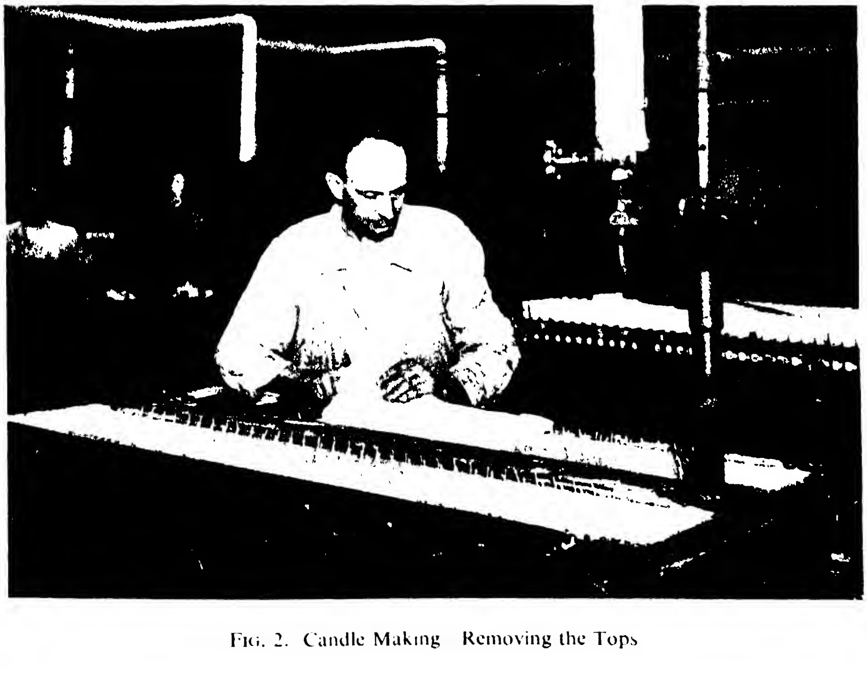


FIG. 2. Candle Making—Removing the Tops

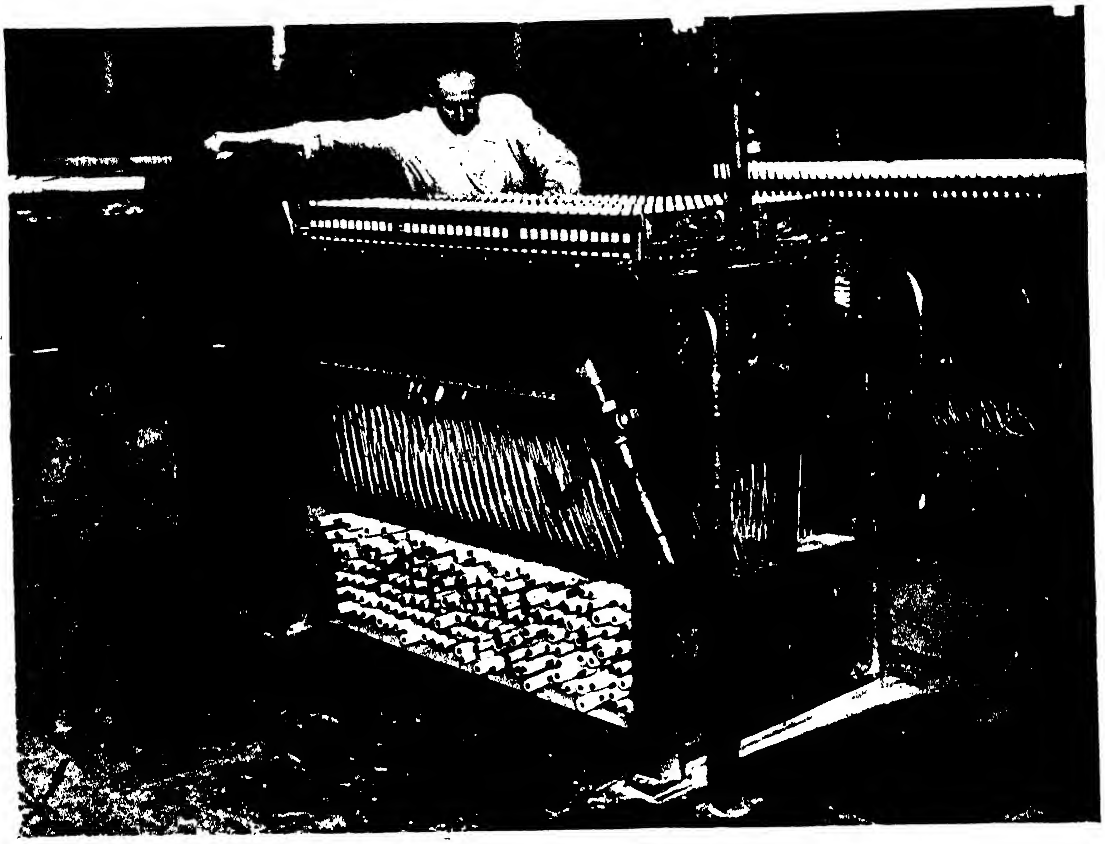


FIG. 3. Candle Making—Winding up

FIG. 4. Moulding Machine for Night Lights

wax and wick must be carefully chosen to suit these conditions.

The wax should have a melting-point low enough to ensure that the small flame can melt the contents of the case under ordinary circumstances. At the same time, the question of storage has to be borne in mind, so that the lights can be kept in stock for some time under reasonable conditions without damage.

In this, and other countries with a similar climate, wax of melting-point 118/119° F. is commonly used, but it cannot be expected to withstand all the widely varying conditions that may be met with. On a very cold night, if the light is in a cold position, about 20–5% of the wax may be unconsumed. On the other hand, during a hot summer the lights may lose their shape unless storage conditions are cool.

All waxes of this melting-point are not suitable for night-lights, probably due to different treatment at the various refineries, but they can usually be made satisfactory by further treatment. They must not contain the slightest trace of suspended matter, as this will choke the wick and cause a very small flame.

The wick is made from fine quality yarn, like sewing cotton, and, after plaiting, &c., as with candle wick, it is given a coating of wax to stiffen it, so that it is easier to handle and easier to light, and is then cut into suitable lengths. It is important that the wick should stand upright when burning, particularly when the whole of the wax is melted, and it must burn regularly, so that the timing is correct. This can only be ensured by continually checking the burning of the lights.

The process of moulding night-lights is similar to that for candles, except that they are made without wicks. In the centre of the mould is a pin which projects nearly to the top, and this makes a hole into which the wick is inserted later by hand. Various suggestions have been made to produce the moulds with wicks, but none of them have proved practicable. Some moulds are made by stamping from a block of wax, but in this method the wax must be warm and plastic.

Fig. 4 shows details of a moulding machine.

The paper cases are made in various ways. Some are made partly by machine and partly by hand, while others, especially those for lights used with water, are sometimes made completely by machine. The joints in the case for water-lights, as the first type are often called, must be carefully stuck together, or the water will travel up these and chill the wax, so that it is not completely melted, and thus cause short timing.

In paper-cased lights of type 1 the tin support or sustainer is threaded on a length of wick, which is stuck to the bottom of the case with wax, similar to sealing-wax. The hole in the mould is completed by means of a heated piercer, and the mould is then placed over the wick in the case. In the other two types the wick is bent underneath the sustainer and flattened out to prevent its withdrawal. The lights are then either placed in paper cases or packed for burning in glasses or other containers.

Tapers

Tapers are made by passing cotton yarn, which is usually in lengths of from 600 to 1,800 yards, backwards and forwards through a bath of wax, and then through dies, until the desired thickness is attained. After cutting to the required length they are feathered to facilitate lighting, and packed either in bundles or cartons. The percentage of cotton is much higher in tapers than in candles, 15–20% on the finished article, in order to prevent the melted wax from dropping. The colours used are the same as for candles.

ASPHALTIC BITUMEN, COKE, AND REFINERY RESIDUES

THE MANUFACTURE OF ASPHALTIC BITUMEN

By **W. W. GOULSTON, B.A., B.Sc., A.I.C.**
Asiatic Petroleum Company, Ltd.

Introduction

ASPHALTIC bitumen is normally obtained as a residue from suitable types of crude oil by carrying the distillation beyond the stage where gas oil is distilled off. The distillation is continued until the residue has the properties required for the particular grade of asphaltic bitumen which is desired. The quality of the product is usually controlled by its 'penetration' as measured by the depth in millimetres to which a loaded needle will penetrate in 5 sec. The penetration is usually carried out at 25° C. (or 77° F.) with a load of 100 g. on the needle. The various methods of distillation which are usually applied to crude oil are available for the production of asphaltic bitumen with such modifications as may be necessary for operating at a higher temperature and handling a product which is solid or semi-solid at ordinary temperatures.

It is often found convenient to use topped crude as the feed to the plant for the production of asphaltic bitumen, and in certain cases cracked residuum of a suitable type may be used as a starting material for this purpose. Cracked residuum is usually available at a high temperature, so that considerable economy in fuel consumption can be effected if suitable grades of asphaltic bitumen can be made from this material.

Another source of asphaltic bitumen is the acid tar obtained in the treatment of lubricating oils with sulphuric acid. It is stated that the asphaltic bitumen produced from this source has been used successfully for road work.

The introduction of the use of solvents for treating lubricating oils has given rise to methods of 'de-asphaltizing' which can be used as a source of asphaltic bitumen. The use of solvents for the production of asphaltic bitumen has the advantage of enabling one to control the type of material obtained in a way which is not possible with ordinary methods of distillation. The product made by this method is sometimes referred to as 'synthetic' asphaltic bitumen.

Influence of Base Material

The grade of asphaltic bitumen is usually controlled by the penetration at 25° C., and when the material is produced from certain crude oils the other properties of the asphaltic bitumen, such as melting-point, are usually of the same order. This is by no means the case for all crude oils from which asphaltic bitumen can be made.

When asphaltic bitumen was first made from crude petroleum, the material was used as a binding medium for the construction of roads and largely replaced natural asphalt which was used for that purpose. The crude petroleum used was of Mexican origin, and the asphaltic bitumen made from this source became the standard of the quality desired for road making. Later on, it was found that asphaltic bitumen made from crude oils of other origin also gave satisfactory results when used for road making, and this widened the scope of the source of crude petroleum suitable for the manufacture of asphaltic bitumen for this purpose.

The analytical figures for 60/70 grade of asphaltic bitumens shown in Table I give some idea of the possible variation in the properties of the material made by ordinary distillation from some crude oils normally used for this purpose. There is a certain variation in the types of crude oil obtained in each particular country; the asphaltic bitumens given in Table I were produced from some typical examples of crude oil from various sources. The asphaltic bitumens shown in this table are all perfectly suitable for use as road binders.

TABLE I

	Mexican	*Venezuelan*	*Californian*
Penetration at 25° C., mm.	65	65	62
Ductility at 25° C., cm.	>100	>100	>100
Melting-point (R. & B.), ° C.	52	50·5	46·5
Viscosity (centistokes) at 150° C.	400	250	125
Solubility in 60/80 spirit, %	78·4	86·3	93·2
Loss on heating (5 hr. at 163° C.), %	0·2	nil	0·03
Drop in penetration after heating in last test, %	10	6	7

Although the application to road building is the largest outlet for asphaltic bitumen, a considerable proportion of the production is used for other purposes. For some purposes, such as roofing felt and pipe coating, it is necessary to combine the properties of high melting-point with flexibility, or comparatively high penetration. In such cases, a 'blown' asphaltic bitumen is used, that is, the product made by oxidizing the straight-run residue by blowing air through it under suitable conditions. For other applications, such as binding material for briquettes, it is preferable to have a combination of low melting-point and brittleness or low penetration. For these purposes, straight-run residues from crude oils yielding suitable materials for road making can be used, but it is found that cracking coil tars give more suitable products when distilled to the required penetration.

The relation between the penetration and the melting-point gives a useful method of classifying the types of asphaltic bitumen, particularly with regard to their suitability for certain industrial applications. In a paper presented to the American Chemical Society in 1935, A. Holmes and J. O. Collins [6] propose numerical magnitudes for the melting-point/penetration index for asphaltic bitumens from various sources. They assume a figure of 100 for Mexican asphaltic bitumen and zero for petroleum pitch from a cracking coil tar. Blown asphaltic bitumen would give a penetration index of over 150, while coal-tar pitch would have a penetration index below zero. By means of this index one can judge for which purpose a particular type of asphaltic bitumen is most suitable. If a certain type of crude oil yields asphaltic bitumen of penetration index too low for use as a road binder, this can be improved by the application of 'blowing' to the extent required to produce a material of suitable penetration index.

Certain crude oils yield asphaltic bitumens having little or no matter insoluble in aromatic-free spirit of boiling range 60–80° C., that is, containing practically no asphaltenes. Such asphaltic bitumens are light in colour when viewed through thin sections and can be used for the preparation of coloured bituminous products, as they can be pigmented quite freely.

Manufacture by Distillation

The production of asphaltic bitumen by distillation from crude oil or topped crude is carried out either under atmospheric pressure or under reduced pressure or 'vacuum'. The use of reduced pressure is advisable when producing hard grades of penetration below 20 or when the overhead distillates are to be used for the manufacture of lubricating oils. Although very little 'cracking' takes place when making the usual paving grades having penetrations from 45/55 up to 180/200, the amount of cracking increases with the higher temperatures necessary for the production of harder grades. The use of reduced pressure ensures that the harder grades of asphaltic bitumen are produced without deterioration in properties and that the overhead distillates can be used for the production of suitable lubricating oils. It is also found that the use of reduced pressure effects a considerable reduction in fuel consumption owing to the lower distillation temperature required and the large reduction in distillation steam. The lower fuel consumption on the vacuum plant may well repay the extra cost of erecting such a unit compared with the cost of an atmospheric plant of the same capacity.

Batch Still. The early plants for the production of asphaltic bitumen were of the batch-still type similar to the early batch crude-oil shell stills. The charge of crude oil was distilled down to a residue having the required penetration for the grade of product desired, steam being used in large quantities to prevent cracking. The use of batch stills for this purpose has the same disadvantages as in the case of crude oil distillation; they have been largely superseded by continuous shell stills and, more recently, by pipe stills. For plants of very small capacity where a large number of grades are required, and where storage for finished products is very limited, the use of one or two batch stills might be desirable, but this method of manufacture is very costly compared with the modern pipe-still plant.

Continuous Battery. The use of a continuous battery of shell stills is quite familiar for the distillation of crude oil, where the last still of the battery contains the residue which is drawn off continuously through heat exchangers to receiving tanks. By suitably adjusting the temperatures of the last stills of the battery, the distillation can be carried out so as to produce the required grade of asphaltic bitumen in the last still. This type of plant is not suitable for rapid changes in the grades of asphaltic bitumen produced, and is nowadays only used for the production of lubricating oil distillates where the asphaltic bitumen made is normally of a constant grade over long periods. Continuous batteries are not used when pipe stills are available; even for the production of lubricating oils under reduced pressure, modern pipe stills are now usually erected.

Pipe Still. The pipe-still unit is the modern type of plant used for the distillation of crude petroleum and of petroleum residues. This type of plant consists essentially of a pipe heater, in which the oil is heated in a pipe coil set in a suitable furnace, and a fractionating column in which the heated oil is split up into the desired overhead fractions as distillates, and a residue taken from the bottom of the column. For the manufacture of asphaltic bitumen the charge to the still may be crude oil, or a 'topped crude', that is, the residue obtained from crude oil after the fractions up to gas oil have been removed by distillation on another plant. The residue taken from the bottom of the fractionating column is the asphaltic bitumen required and this is passed through suitable heat exchangers to receiving tanks.

The chief difference in operating conditions between pipe stills and shell stills is that the oil passes through the heating zone in a much shorter time in the former than in the latter. The effect of subjecting the oil to high temperatures for a long period in shell stills is shown clearly in the figures given in Table II, taken from a paper by A. Balada in 1933 [2], which shows the analysis of two samples of asphaltic bitumen made from the same crude material on each of the two types of plant.

TABLE II

	Shell still		*Pipe still*	
Softening-point (K–S), ° C.	38	42	38	42
Flash-point, ° C.	300	300	336	336
Penetration at 25° C.	123	81	58	35
Ductility at 25° C. cm.	32	16	+100	90

The difference in the two types of asphaltic bitumen is very marked in this case. The asphaltic bitumen produced in the shell still has a much higher melting-point/penetration index and is generally of a more 'blown' character. This is confirmed by the lower ductility of the shell-still product.

There are various modifications of asphaltic bitumen plants which have been designed to suit certain conditions depending on the type of crude oil or topped crude available and the local arrangements of other plants in the refinery. A description of some typical asphaltic bitumen plants will cover most of the pipe-still plants used at the present day for this purpose. The various types may be enumerated as follows: (i) atmospheric with evaporator, (ii) atmospheric without evaporator, (iii) vacuum plant, (iv) two-stage atmospheric and vacuum, (v) without heater.

(i) **Atmospheric Unit with Evaporator.** This type of plant, illustrated diagrammatically in Fig. 1, was used before the modern large fractionating towers became standard practice. It is derived from the Trumble type of pipe-still plant used for topping crude oil.

The crude-oil charge is drawn from a crude-oil supply-tank through a 6-in. steam-jacketed line to the crude-feed pump. A suitable pump for this purpose is a steam-jacketed rotary pump direct-driven by a high speed steam engine. The crude oil, which usually has a high viscosity, is kept sufficiently heated for ease of pumping; in the case of heavy Mexican crude, the temperature is maintained at about 40° to 50° C. by means of 2-in. steam coils in the supply tank. The feed pump delivers the crude oil through a suitable heat exchanger to the pipe heater, which is of the convection type, the crude-oil inlet to the heater being at the top of the tube bank so that the crude is heated in counter-current with the flue gases. The crude oil leaves the pipe heater at a temperature depending on the grade of asphaltic bitumen required and passes into the evaporator where the pressure drops and the vapours are flashed off. There are three or four stripping trays below the oil inlet and the stripping of the residue is assisted with superheated steam at 280–300° C. supplied through a spider in the bottom section of the evaporator. The residue, which is the asphaltic bitumen required, is drawn off from the bottom of the evaporator, a constant level being kept in the evaporator by means of a constant level device. The asphaltic bitumen flows from the evaporator through the heat exchangers where it is cooled to 160–180° C. by the crude oil charge. From the heat exchangers, the asphaltic bitumen flows by gravity to two receiving tanks and is pumped from these tanks to the storage tanks.

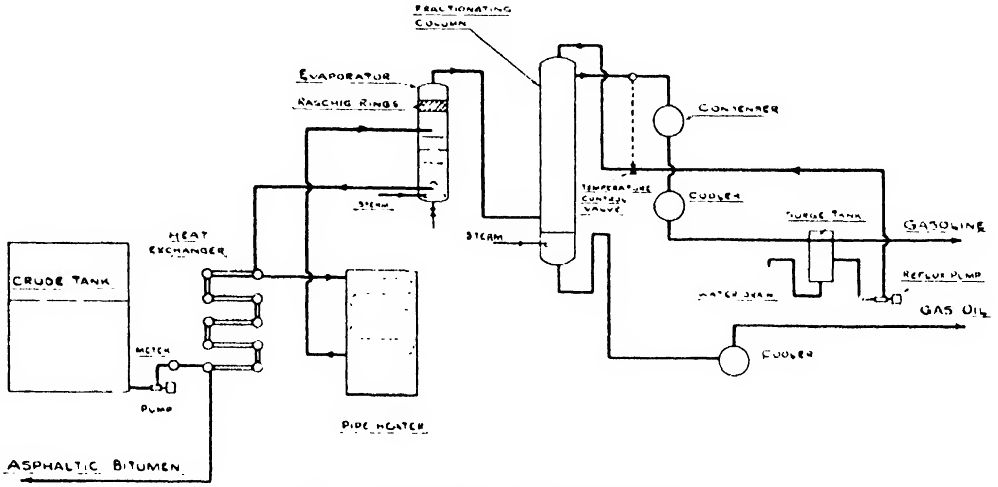


FIG. 1. Atmospheric unit with evaporator.

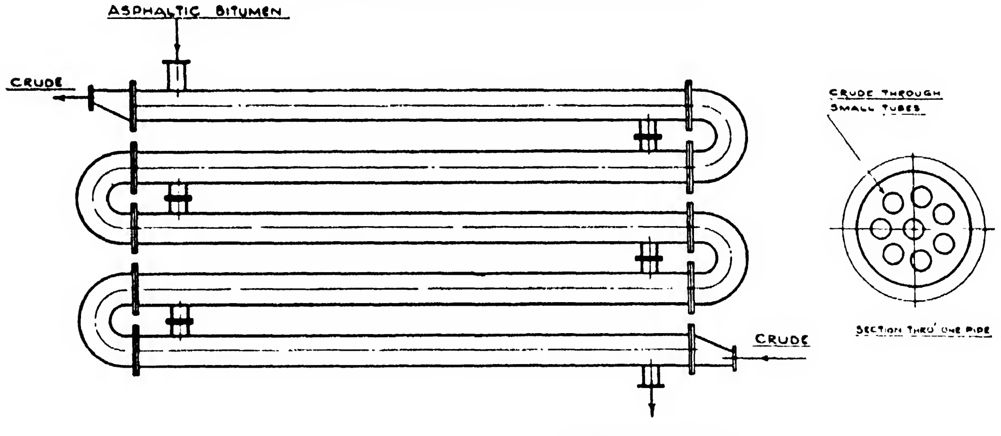


FIG. 2. Asphaltic bitumen heat exchanger.

The vapours flashed off in the evaporator pass through a layer of Raschig rings which acts as a mist extractor, to the fractionating column where suitable separation can be made of the required distillate cuts. In the case of heavy Mexican crude oil it is usual to take a gasoline cut of required end-point from the top of the column and the bottom of the column yields a gas oil or Diesel oil. The end-point of the gasoline from the top of the column is controlled by refluxing part of the condensed gasoline, the rate of reflux being subjected to a temperature controller which keeps a constant temperature at the top of the column. The gasoline reflux is pumped to the top of the column by means of a centrifugal pump which can be controlled either on the steam supply to the pump or by means of a by-pass on the delivery from the pump.

The evaporator is a vertical cylinder, 22 ft. in height and 6 ft. in diameter with dished ends. The hot oil from the pipe heater enters the side of the vessel about 8 ft. 6 in. from the top through a 6-in. line. Immediately above the oil inlet a layer of Raschig rings, about 2½ ft. in height, is supported on an expanded metal grid. The vapours leave the vessel through a 12-in. outlet in the centre of the top cover. The asphaltic bitumen leaves through a 6-in. outlet placed on the side of the vessel about 2 ft. 6 in. from the bottom, an internal standpipe being fitted to maintain a constant level. Below the oil inlet there are three or four trays of the 'dish and doughnut' type and beneath the bottom tray there are two 2-in. steam spiders through which superheated steam is supplied. The vessel is insulated with Highpor bricks cement rendered.

The heat exchangers illustrated in Fig. 2 are of a type particularly suitable for use with asphaltic bitumen. They consist of a number of sections of 12-in. pipe about 21 ft. in length, in each of which are fitted 8 tubes of 2½ in. diameter running parallel with the length of the sections. The length of the tubes between the plates is 20 ft. 9 in. and the effective cooling surface of a heat exchanger having ten sections is 1,058 sq. ft. The connexions for asphaltic bitumen are 6 in. in diameter and those for crude oil are 4 in. in diameter. One heat exchanger of these dimensions is kept in operation and a second is held as a spare. The asphaltic bitumen enters at the top and passes through the shell, the crude oil entering at the bottom passes through the tubes.

The fractionating column is 6 ft. 7 in. in diameter and 39 ft. 6 in. in height. It contains 39 trays, of which 8 are below the vapour inlet. The bottom distillates are drawn off from the column through a 4-in. seal pipe, while the vapours leave the top of the column through an 18-in. outlet on the side about 2 ft. 6 in. from the top, the vapour line from this point being reduced to 12 in. in diameter. Two 1-in. steam spiders are fitted in the bottom section for supplying superheated steam. The column is lagged with asbestos mattresses protected with galvanized-iron sheeting.

TABLE III

Operating Conditions for Atmospheric Unit

Penetration of asphaltic bitumen	180/200	60/70	45/55
Temperatures, ° C.:			
Crude to heat exchanger	50	50	50
Crude to heater	115	125	125
Crude to evaporator	320	360	370
Asphaltic bitumen to receivers	160	180	190
Flue gas at base of stack	340	380	390
Pressures, lb. per sq. in.:			
Crude to heat exchanger	60	75	85
Crude to heater	55	70	80
Intake Mexican Crude, tons per day	280	220	210

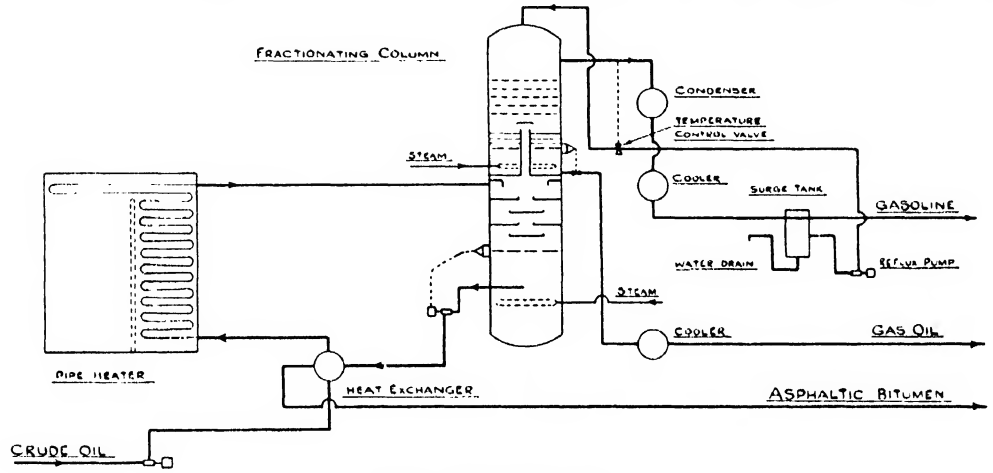


FIG. 3. Atmospheric unit.

The average working conditions of the plant when making the standard paving grades of asphaltic bitumen are given above in Table III.

(ii) **Atmospheric Unit without Evaporator.** This type of plant consists essentially of a pipe heater and a fractionating column, the evaporator of plant (i) being incorporated in the bottom section of the fractionating column. Fig. 3 illustrates diagrammatically a plant of this type.

The crude oil is pumped through residue heat exchangers where it is heated by the asphaltic bitumen leaving the plant. The heated crude oil passes through a pipe heater where it leaves at a temperature depending on the grade of asphaltic bitumen required. The heated crude oil enters the lower part of the fractionating column, which is the vaporizing section where the crude oil is flashed, the vapours rising through the upper fractionating section and the residue descending over a series of trays in the stripping section to the bottom of the column where the asphaltic bitumen is continuously drawn off, passing through the heat exchangers to storage. Super-heated steam is supplied at the bottom of the column below the stripping trays, and a constant-level device keeps a level of residue in the bottom of the column.

The vapours flashed from the crude oil rise through a series of bubble trays in the fractionating section of the column. Superheated steam is supplied to the bottom of the fractionating section where a gas-oil distillate is taken off as a side cut. From the top of the column gasoline is taken off having the required end-point, which is regulated by the temperature controller at the top of the column.

When a kerosine cut is required, this can be taken as a side cut from a suitable tray between the top of the column and the bottom of the fractionating section, a steam stripping section being incorporated at the required tray, similar to that used where the gas oil is taken off.

If the feed to the plant is a topped crude, gas oil is taken from the top of the fractionating column and a lubricating distillate or Diesel oil is taken from the bottom of the fractionating section.

(iii) **Vacuum Plant.** Both plants (i) and (ii) may be arranged to operate under reduced pressure. This modification is particularly suitable for the distillation of topped crude. Fig. 4 illustrates diagrammatically a plant with an evaporator arranged with suitable means of maintaining reduced pressure. In this plant the topped crude is fed to a vapour heat exchanger, where it is warmed by vapours from the fractionating column. The feed then passes through a series of residue heat exchangers where it is further heated by the hot asphaltic bitumen leaving the bottom of the evaporator. The heated feed is then pumped through a pipe heater of suitable capacity where the feed is heated up to a temperature depending on the grade of asphaltic bitumen required. This temperature is controlled by keeping the firing conditions steady and manipulating the inlet valve to the heater. The feed pump of a rotary type is kept running at constant speed and any excess of feed not taken through the inlet valve to the pipe heater is by-passed to the suction side of the pump. By this method the temperature of the oil leaving the pipe still can be kept within one or two degrees of the temperature required. On this plant, a change of grade is simply effected by a small alteration on the inlet valve to the pipe heater, all the other conditions then adjusting themselves so as to obtain the proper temperature of the oil at the outlet of the pipe heater corresponding to the grade of asphaltic bitumen required.

The heated oil at the desired transfer temperature passes to the evaporator, a vertical cylindrical vessel, 25 ft. in height and 6 ft. in diameter, where it enters at a point about two-thirds the way up and descends over a series of 6 stripping trays below which superheated steam is supplied through a spider. The evaporator is under a pressure of about 2 in. of mercury and there is a good separation between the residual asphaltic bitumen and the distillate vapours. The asphaltic bitumen is removed from the bottom of the evaporator by means of a steam-jacketed rotary pump which pumps the product through the heat exchangers to storage. A constant level of asphaltic bitumen is maintained in the bottom of the evaporator by means of an automatic level controller.

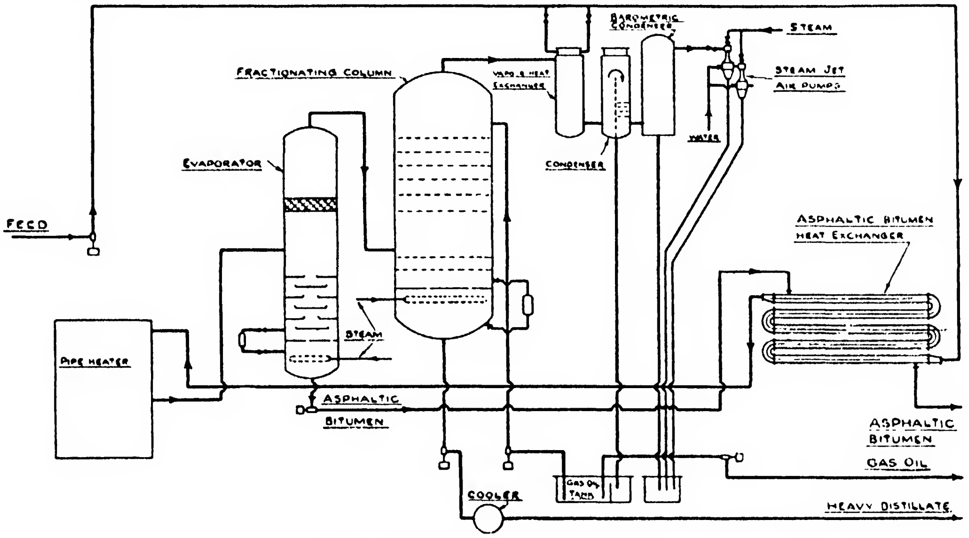


FIG. 4. Vacuum unit with evaporator.

The mixture of oil vapours and steam passes upwards through a layer of Raschig or Lessing rings and leaves the evaporator by a 30-in. vapour line passing to a fractionating column 45 ft. in height and 12 ft. in diameter. There are 2 stripping trays below the inlet to the column and 6 bubble-cap trays above the inlet, and superheated steam is fed into the bottom of the column to assist in stripping the residue. The top of the column yields gas oil and part of this product is used as reflux for controlling the temperature at the top of the column, the reflux being supplied by a centrifugal pump and the amount of reflux regulated by a temperature controller at the top of the column. The bottom of the fractionating column gives a lubricating oil distillate which is pumped continuously away through water coolers to storage, a constant level being maintained at the bottom of the column.

From the top of the fractionating column the mixture of gas-oil vapours and steam passes through a vapour to a crude heat exchanger, and then to a condenser cooled by water regulated so as to condense all the gas oil but not the steam. The condensed gas oil passes to a surge tank where part of the gas oil is supplied to the reflux pump and the balance pumped to storage. The uncondensed steam from the gas-oil condenser passes to a water-cooled barometric condenser which is a vertical cylindrical vessel about 40 ft. above ground level. The steam and any uncondensed vapours pass through a series of horizontal baffle plates in the barometric condenser and meet a descending stream of cold water which condenses the steam. The mixture of cooling water and condensate passes from the barometric condenser through a long vertical pipe which is sealed by a water seal at ground level. The top of the barometric condenser is connected to a steam-jet air pump or a vacuum pump which maintains the desired vacuum on the whole plant. The operating conditions for a plant of this type, distilling Venezuelan topped crude, are given in Table IV.

A vacuum plant in which no evaporator is used, corresponding to plant (ii), is illustrated diagrammatically in Fig. 5. The principle of operating this type of plant is very similar to that described under plant (ii). The design of the two types of plants is also similar, except that allowance must be made for the larger volume occupied by the vapours under reduced pressure, so that a larger diameter is required for the same capacity in the vapour space of the fractionating column and the vapour lines must be of correspondingly larger diameter.

The operating conditions of this type of plant are given in Table V, the figures being taken from an article by W. T. Ziegenhain [10] in the *Oil and Gas Journal* in 1933.

TABLE IV

Operating Conditions for Vacuum Unit with Evaporator

Grade of asphaltic bitumen	180/200	45/55
Temperatures, ° C.:		
Feed ex pump	52	52
„ vapour heat exchanger	111	124
„ asphaltic bitumen heat exchanger	160	179
„ pipe heater	307	352
Asphaltic bitumen ex evaporator	280	311
„ „ heat exchanger	188	189
Vapour ex evaporator	284	330
„ fractionating column	205	212
„ vapour heat exchanger	164	174
Pressures, mm. Hg absolute pressure:		
In ejector	20	14
At top of fractionating column	22	18
At bottom „ „	28	31
In evaporator	33	38
Intake of feed, tons per day	432	324
Ratio of steam to total distillate	1:20·0	

TABLE V

Operating Conditions for Vacuum Unit

Temperatures, ° C.:	
Feed inlet to pipe heater	232–316
„ outlet „	371–443
Top bubble-tray of fractionating column	316
Pressure at top of column	38–50 mm. of mercury.
Yields of Products:	
Gas oil	24%
Lubricating oil distillate	45%
Asphaltic bitumen 100 penetration	30%
Loss	1%
	100%

The feed to the plant is 20 gravity (sp. gr. at 15° C. O. 934) topped crude and the products made are gas oil, lubricating oil distillate, and asphaltic bitumen.

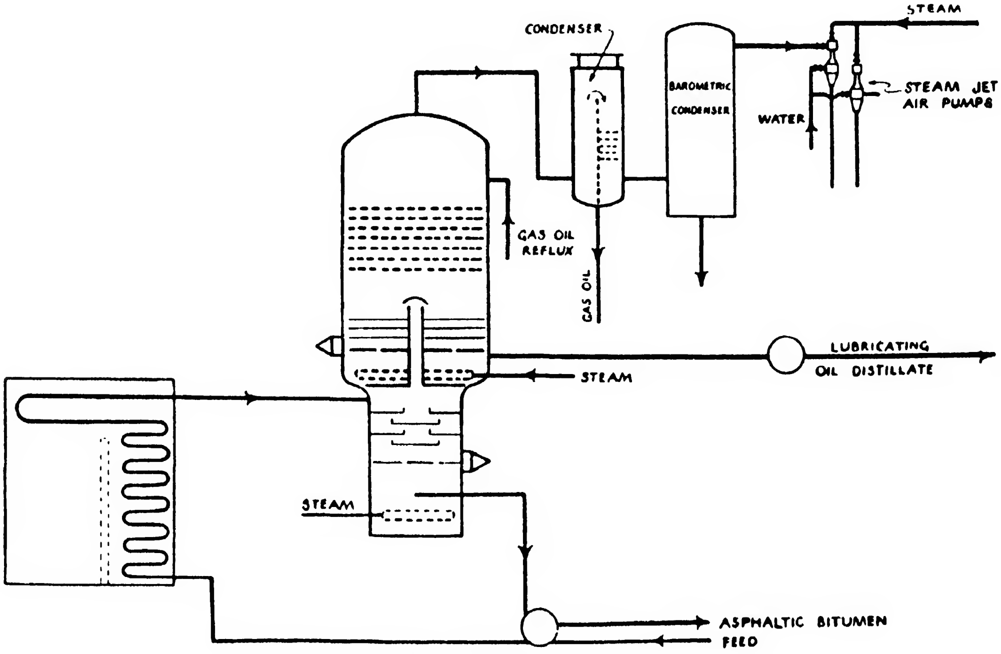


FIG. 5. Vacuum unit.

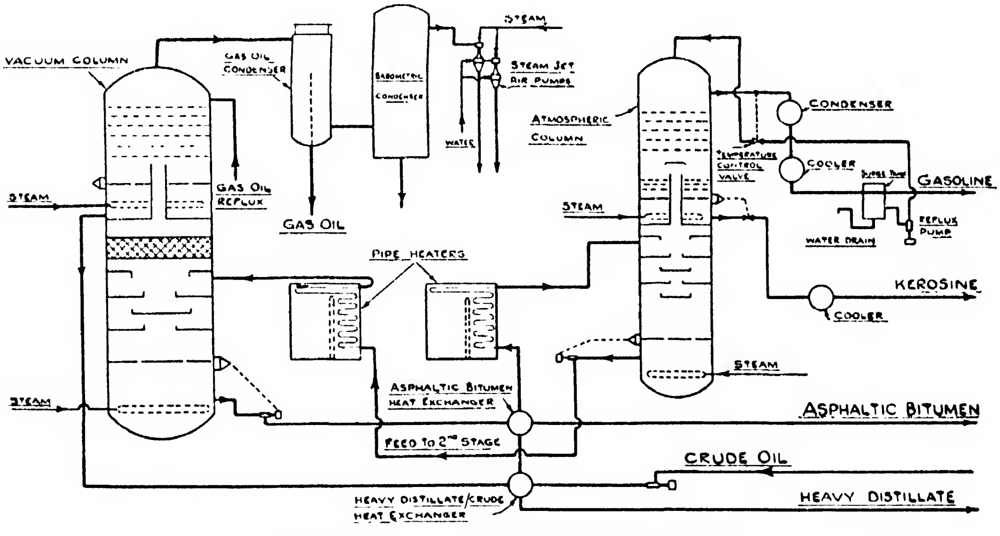


FIG. 6. Two-stage atmospheric and vacuum unit.

(iv) **Two-stage Atmospheric and Vacuum Unit.** This type of plant is suitable for the direct distillation of crude oil down to a residue of asphaltic bitumen. In the atmospheric stage the crude oil is topped, taking off gasoline and kerosine and producing a residue which is further distilled in the second stage under vacuum. In the vacuum stage the required asphaltic bitumen is obtained as a residue and the overhead distillates consist of gas oil and lubricating oils or Diesel oil depending on the type of crude oil treated.

A plant of this type is shown diagrammatically in Fig. 6.

In the atmospheric stage the crude oil is pumped through distillate-crude oil heat-exchangers, then through asphaltic bitumen-crude oil heat-exchangers to a pipe heater. The heated crude oil passes from the pipe heater to the atmospheric fractionating column. This column is divided into two sections, the lower part acting as an evaporator where the crude oil is flashed, and the residue passes over a series of stripping trays, superheated steam being admitted through a spider at the bottom of the column. The vapours rise through a series of bubble-plates to the top of the column. From the top, gasoline of required end-point is taken off, the temperature at the top of the column being kept constant by refluxing gasoline regulated by a temperature controller. A kerosine cut can be taken off as a side cut from a suitable tray in the fractionating section of the column. Additional superheated steam may be supplied in the column just below the kerosine outlet so as to improve the kerosine cut.

The topped crude residue at the bottom of the atmospheric fractionating column is drawn off by a pump and fed to the second pipe heater where the oil is heated to the temperature necessary for the particular grade of asphaltic bitumen required. The heated oil leaves the heater and passes to the vacuum fractionating column where it is flashed, and the residue passes down over a series of stripping trays, superheated steam being supplied through a spider beneath the bottom tray to assist in stripping the residue. This residue, which is the required grade of asphaltic bitumen, passes through crude oil heat exchangers and then to storage. A constant level of the residue is kept in the bottom of the column by means of a float controller.

The vapours separated from the residue pass up above the oil inlet to the column through 3 ft. of Raschig or Lessing rings, then through a series of bubble-trays. A light gas oil is taken from the top of the column and a heavy gas oil or lubricating oil distillate is taken as a side-cut at a point just above the layer of Raschig rings. A temperature controller regulates the reflux of gas oil to the top of the column to maintain a constant temperature. The steam and uncondensed vapour leaving the water-cooled gas oil-condenser passes to a barometric condenser which is connected up to a steam-jet air pump or a vacuum pump.

When distilling a heavy Mexican crude oil on this plant the light gas oil and heavy distillate are blended to produce Diesel oil and the yields of products are shown in Table VI.

TABLE VI

Products from Heavy Mexican Crude Oil

Grade of asphaltic bitumen	180/200	45/55
Gasoline % by weight	3·5	3·5
Kerosine „	4·0	4·0
Diesel oil „	19·3	23·3
Asphaltic bitumen, % by weight	72·0	68·0
Loss (including water) „	1·2	1·2
	100·0	100·0

The operating conditions are given in Table VII, when producing 180/200 and 45/55 grades of asphaltic bitumen.

TABLE VII

Operating Conditions for Two-Stage Unit

Grade of asphaltic bitumen	180/200	45/55
Temperature, ° C.:		
Crude to distillate heat exchangers	56	58
„ „ asphaltic bitumen heat exchs.	89	100
Crude to first-stage heater	118	146
Atmospheric column inlet	214	222
Feed to second stage heater	196	206
Vacuum column inlet	240	306
Asphaltic bitumen to heat exchangers	236	284
„ „ „ storage	184	212
Pressures—mm. Hg absolute pressure:		
Barometric condenser	14	14
Vapour line ex condenser	16	16
„ „ column	16	18
At hot oil inlet to column	22	28
Intake of crude oil, tons per day	820	740
Superheated steam to atmos. column, lb. per hr.	182	182
Ratio of steam/distillate „ „	1:24	1:24
Superheated steam to vacuum column, lb. per hr.	650	714
Ratio of steam/distillate „ „	1:18·3	1:25

(v) **Unit without Heater.** In certain cases a residuum is available leaving a plant at a sufficiently high temperature for further distillation to take place by the addition of superheated steam and by the application of reduced pressure. A particular example of this condition is the case of residuum leaving a cracking plant under high pressure. If this cracked residuum is passed to a fractionating column under reduced pressure and superheated steam added at the base of the column, it is possible to produce asphaltic bitumen which can be drawn from the bottom of the fractionating column.

Fig. 7 illustrates diagrammatically an arrangement for a plant operating under these conditions. The cracked residue from the cracking plant is taken through a 2-in. steam-jacketed line to a horizontal cylindrical surge tank 10 ft. in diameter and 15 ft. long. The low pressure in the fractionating column draws the feed from the surge tank continuously into the column, the flow being hand regulated by a 3-in. gate valve. The feed, at a temperature of about 430° C., enters the column about two-thirds the way up. Below the feed inlet there are 8 bubble-trays, the bubble-caps being arranged for very small submergence, so as to have a low pressure drop through the column. At the bottom of the column, superheated steam is supplied through a spider to assist in stripping the residue. The asphaltic bitumen is drawn off from the bottom of the column by means of a pump which is regulated by a float controller keeping a constant level in the bottom of the column. The asphaltic bitumen is passed through a series of coolers and then to storage.

Above the feed inlet to the column there are 8 mist extractor plates, and the cracked distillate is taken off as a single overhead cut from the top of the column. As no fractionation is required, beyond stripping of the asphaltic bitumen, no additional reflux is fed to the top of the column. The vapour leaves the top of the column through an 18-in. insulated line which is arranged in a large loop as the temperature of the vapour is high. The vapour is condensed under vacuum and pumped to storage.

The penetration of the asphaltic bitumen produced is controlled by regulating the volume of superheated steam supplied to the column. Further control of the penetration may be obtained by varying the absolute pressure in the column and also by regulating the quantity of feed to the column.

The asphaltic bitumen is cooled by means of a circulating system of gas oil supplied from a surge tank, the heated gas oil being cooled with water and returned to the surge tank. By this means the rate of cooling of the asphaltic bitumen is controlled so that no over-cooling and congealing takes place.

The asphalt cooler consists of 10 sections of multitubular coolers arranged in 2 vertical banks of 5 each in series flow. The shells are 10 in. in diameter and 18 ft. long. They are fitted with steel caps, which hold in position 12 2-in. tubes in each section arranged in 3 passes. Asphaltic bitumen passes inside the tubes and gas oil flows through the shell outside the tubes. The return bends for the asphaltic bitumen are steam jacketed. The total effective heat-transfer surface of the cooler is 1,116 sq. ft. The gas-oil cooler is made up of four sections of similar multitubular construction, except that the caps are of semi-steel. In this cooler the gas oil passes inside the tubes and the shell serves as a water or steam jacket as desired. The total effective heat-transfer surface of this unit is 446 sq. ft. When starting up the plant it is desirable to use steam for heating up the gas oil to a temperature of 120° C. When the asphaltic bitumen is being produced at a normal rate the gas oil-cooler is cooled with water.

The yields and properties of various grades of asphaltic bitumen made on this type of plant from cracked residuum are given in Table VIII.

TABLE VIII

Unit Without Heater

Feed intake, barrels per day	744	720	727
Yield asphaltic bitumen, % (volume)	90	74	66·5
„ distillate, %	10	26	33·5
Melting-point (R. & B.), ° C.	36	59	83
Penetration at 25° C.	260	9	2

Fuel Consumption for Distillation.

One of the most important items of expenditure in the manufacture of asphaltic bitumen by distillation is the consumption of fuel for heating purposes. The fuel is consumed directly for heating the oil in the pipe heater and indirectly, in the form of steam, to assist the distillation and fractionation. Indirect fuel is also used, in the form of steam, electricity or oil, for heating tanks and pipelines and for driving pumps. In Table IX the figures for fuel consumption are taken from actual operation of atmospheric and vacuum plants when distilling heavy Mexican crude oil and Venezuelan topped crude oil.

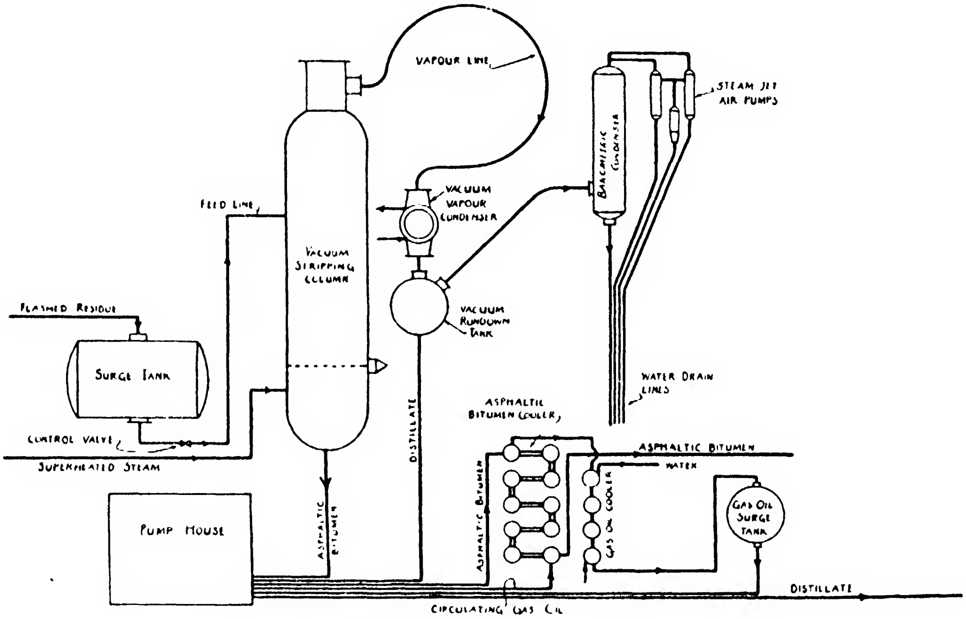


FIG. 7. Unit without heater.

TABLE IX

Fuel Consumption for Manufacture of Asphaltic Bitumen by Distillation

	Mexican Crude Oil		*Venezuelan Topped Crude Oil*	
% on intake	*Atmospheric*	*Vacuum*	*Atmospheric*	*Vacuum*
Direct fuel	2·7	1·6	3·0	2·0
Indirect fuel—distillation	0·45	0·13	0·75	0·25
Indirect fuel—other purposes	1·49	1·68	1·49	1·68
Total fuel consumption	4·64	3·41	5·24	3·93

It is evident from the above figures that there is a saving of about one-third in the direct fuel consumption when using a vacuum plant compared with an atmospheric plant. However, there is no great saving in the indirect fuel consumption, as the decrease in steam required for distillation is almost covered by the additional fuel required for operating the vacuum pumps. Of the total fuel consumed, there is a saving of about one-quarter of the fuel required, if a vacuum plant is used.

Manufacture from Acid Sludge

Asphaltic bitumen may be recovered from the acid sludge obtained by the treatment of asphaltic or mixed base lubricating oil distillates with concentrated sulphuric acid. The production of asphaltic bitumen by this method is used only to a limited extent and mainly for the purpose of disposing of a waste product which may become a nuisance. (See article by Oliver and Spangler.)

One method of treating the acid sludge is described by H. Abraham [1, 1929]. The acid sludge, mixed with water, is agitated with air and live steam in a lead-lined agitator and the mixture, on settling, separates into three layers. The dilute acid layer settles to the bottom and an oily layer rises to the top, while the middle layer consists of acid tar which solidifies on cooling. The top and bottom layers are removed and the acid tar is further washed with water and agitated with steam and air until all the acid has been removed from the tar. The tar is then heated with superheated steam which causes the distillation of the tar to take place, and this is continued until the residual pitch has the desired penetration.

In a second method, described by C. Baskerville [4] in 1920, the acid sludge is heated up with concentrated sulphuric acid and live steam for an hour or so, when 3 layers are formed. The top layer is separated oil and the bottom layer is concentrated acid, while the middle layer is a pasty mass containing the asphaltic material and 15 to 25% of sulphuric acid. This middle layer of tar is separated and washed with water. The tar is then mixed in a suitable mill with sufficient slaked lime or finely powdered limestone to neutralize any acid present. The heat of reaction, during neutralization, raises the temperature of the mixture sufficiently to make it fluid so that it can be filled into receptacles for distribution. The asphaltic bitumen made in this way contains 10 to 40% of calcium sulphate depending on the amount of free acid present before neutralization [3].

R. de M. Taveau [9] was granted a patent in 1918 for the production of asphaltic bitumen from acid sludge. In this process, the acid sludge is digested with steam and water and the mixture settles into 3 layers. The middle layer, which is acid tar, is emulsified with an excess of sodium hydroxide or sodium carbonate. This emulsion is broken, either by heating to 100° C. or by adding benzene and blowing air through the mixture. By either method of breaking the emulsion, an upper layer is obtained containing, in the first case, oil and asphaltic bitumen, while in the second case, a mixture of oil, asphaltic bitumen, and benzene is obtained. The asphaltic bitumen is then produced by distilling the separated upper layer down to a residue of the required penetration.

Asphaltic bitumen prepared from acid sludge usually has a low melting-point/penetration index and shows lower resistance to weather exposure than normal residual or blown asphaltic bitumen.

Manufacture by Solvents

Asphaltic bitumen can be removed from residual oils by the addition of low-boiling hydrocarbons which cause the precipitation of asphaltic material as a lower layer containing a small amount of the solvent while the remainder of the oil forms a solution as the upper layer. The properties of the asphaltic material separated in this way depend on the nature of the residual oil treated, the type of solvent used, and the conditions under which the treatment is carried out. This method was proposed by the I.G. Farbenindustrie in 1932 [7] for the 'fractional precipitation of asphalts and pitches . . . from crude petroleum, or distillation, cracking or destructive hydrogenation residues obtained from coal, tars or mineral oils'. In this process the residual oil is heated with liquid butane to 50° C. under pressure and the precipitated asphaltic material is separated. The solution of oil in butane is then treated with a mixture of propane and ethane, kept in a liquid state under pressure, when a further amount of asphaltic material is precipitated. The asphaltic bitumen precipitated in these two stages have different properties and the process can be considered as one of fractional precipitation.

The effect of using different solvents to precipitate the asphaltic material is illustrated in the results given by U. B. Bray, C. E. Swift, and D. E. Carr [5] in 1934, who treated a topped crude oil of viscosity 66 sec. Saybolt Universal at 100° F. with a series of light hydrocarbon solvents including ethane, propane, and butane. Some of the results obtained when treating the topped crude with ten volumes of solvent at 80° F. are given in Table X.

Ethane gives a high yield of very soft asphaltic material from this particular residual oil, while butane gives a much lower yield of asphaltic bitumen of very high melting-point. Propane yields an asphaltic material which is fairly near to a normal hard grade of asphaltic bitumen obtained by the distillation of the topped crude oil.

In the refining of lubricating oils, liquid propane is used for a number of purposes, one of which is the removal of asphaltic material from residual oils, or 'de-asphaltizing'.

TABLE X

Properties and Yields of Asphaltic Bitumen Produced by Extraction with Light Hydrocarbon Solvents

Solvent	*Yield of asphaltic bitumen % vol. on topped crude*	*Properties of asphaltic bitumen*			
		Sp. gr. at 60° F.	*Melting-point, ° F.*	*Pen. at 77° F.*	*Ductility at 77° F.*
Ethane . .	89·0	0·98	. .	soft	0
Propane (b.p. −42 to −40° F.) .	25·0	1·063	176	2	0
Butane (b.p. 30 to 36° F.).	11·2	. .	307	0	0

The residual oil is mixed with a suitable quantity of liquid propane at the required temperature and when equilibrium is obtained the mixture separates into two layers, the upper layer containing the de-asphaltized oil in solution in propane and the lower layer consists of the precipitated asphaltic material mixed with a little propane. The propane in the lower layer is removed by evaporation, leaving behind the asphaltic bitumen.

The quality of the asphaltic bitumen produced by this method depends on the nature of the residual oil treated and on the amount of propane used or the solvent ratio. The minimum proportion of propane which will cause a separation into two layers is the critical ratio, and as the proportion of propane is increased beyond the critical ratio, more oil passes from the lower layer to the upper layer until a maximum is reached when further increase in the ratio of propane causes no additional separation. Between the limits of the critical ratio and the optimum propane ratio the precipitated asphaltic bitumen contains decreasing proportions of oil, so that the grade or penetration of the asphaltic bitumen produced can be controlled by the propane ratio used for separation.

The solvent process gives a method of controlling not only the penetration of the asphaltic bitumen but also the type of material produced as measured by the melting-point/penetration index or the change in penetration or viscosity with temperature, that is, the susceptibility. C. Mack [8] in 1933 pointed out that the susceptibility of asphaltic bitumen depends on the chemical composition of the oily constituents and on the change in their viscosity with temperature. If the residual oil normally yields by distillation asphaltic bitumen of high susceptibility, corresponding to low melting-point/penetration index, the asphaltic material precipitated by using the optimum propane ratio can be fluxed with a heavy oil of low susceptibility in order to produce asphaltic bitumen of suitably high melting-point/penetration index.

The method of producing asphaltic bitumen by solvent processes is still largely in the experimental stage. The use of propane for this purpose can only be considered where there is an abundant economic supply of this hydrocarbon.

Under present conditions, the process is generally more expensive than the usual distillation methods, but the increasing use of solvent extraction processes for refining lubricating oils will tend to make the de-asphaltizing of residual oils more general, and as a consequence the production of asphaltic bitumen by this method will acquire commercial importance.

REFERENCES

1. Abraham, H., *Asphalt and Allied Substances*, 3rd ed., 348 (1929).
2. Balada, A., *Chim. et Ind.*, special number, 523 (1933).
3. Baskerville, C. U.S.P. 1,234,985 (1917).
4. —— *Ind. Eng. Chem.* **12,** 30 (1920).
5. Bray, U. B., Swift, C. E., and Carr, D. E. *Refiner*, **13,** 333 (1934).
6. Holmes, A., and Collins, J. O. Amer. Chem. Soc. Meeting (April 1935).
7. I.G. Farbenindustrie, B.P. 409,278 (1932).
8. Mack, C. Asphalt Institute Meeting, Washington (Dec. 1933).
9. Taveau, R. de M. U.S.P. 1,271,387 (July 1918).
10. Ziegenhain, W. T. *Oil and Gas J.* **32** (29), 10 (1933).

BLOWN ASPHALT

By H. B. PULLAR

Vice-President and General Manager, Berry Asphalt Company, Chicago

On 28 April 1893 Francis X. Byerley applied for a patent for the treatment of residuum oil by heating the oil to a pitch-forming, non-coking temperature of about 600° F., and by sucking air through it by means of a suction pump. The apparatus which Byerley used was a closed shell still with a few open air-pipes extending through the top of the shell and within a few inches of the bottom.

Byerley produced various grades of asphalt products from a soft rubber-like consistency to hard pitch with the melting-point varying from 200 to 400° F., which he recommended for paving, roofing, and industrial purposes.

This appears to be the first practical attempt to make air-blown asphalts in the United States.

Because of the fact that Byerley used a light Ohio residuum oil, having a gravity of approximately 22° Bé., and because he maintained this oil at comparatively high temperatures with a small quantity of air, his process was essentially a distillation process, with the air used principally for agitation and to accelerate the distillation. There was, however, no question but that the air did have a chemical effect on the residuum and changed its chemical composition. Byerley was cognizant of this fact and so described it in his patent application.

Because of the unusual characteristics of these Byerley products and the difficulty in manufacturing due to the fire-hazard which accompanied his process comparatively small quantities were used.

On 21 February 1898 G. K. Culmer, who apparently was familiar with the Byerley process, applied for a patent, describing his process as one by which a residuum oil could be chemically changed from a liquid into a semi-solid by forcing a copious amount of air through the heated mass of residuum oil at comparatively low temperatures and below the pitch-forming temperatures described by Byerley, and without any appreciable loss by distillation. The Culmer process, as described, is without doubt the forerunner of the present methods used in air-blowing residua and asphalt products of various types.

In the first practical application of the Culmer patents comparatively small stills holding between 1,000 and 3,000 gal. of residuum oil were used, and the air was introduced into the heated mass of oil by a single perforated pipe laid along the bottom of the still. The air was forced into the mass by means of low-pressure air compressors—the pressure being maintained at approximately 18 lb.—and approximately 10 lb. of air per cu. ft., per ton, per min., forced through the oil.

Because of the quality, character, and light gravity of the residuum used in these early experiments, and because of the poor distribution of air through the oil mass, the time of blowing varied from 20 to 60 hr.

At the time Culmer began his experiments a heavier residuum had become available, and most of the early Culmer experiments were made with an Ohio residuum having a gravity of approximately 18° Bé., which enabled him to produce air-blown asphalts at lower temperatures and without any substantial distillation taking place.

Both the early Byerley and Culmer air-blown asphalts proved unsatisfactory for paving, but were used successfully for industrial purposes—such as blending with rubber, making black paints, mixing with insulating materials, waterproofing, mastic floors, and filler for brick pavements.

On account of the character of the residua used during this period, and because the asphalts produced were short, cheesy, and with little adhesive properties, it was found necessary, in order to obtain satisfactory results, to blend these air-blown residua with natural asphalts—such as Gilsonite—which imparted to the blown asphalts increased stability, better adhesive properties, and greater ductility.

During the early period of making air-blown asphalt the common practice of refining crude oil was by batch distillation, and little attention was given to controlling the qualities of the residuum produced. As a result of these antiquated and now obsolete methods of refining crude, there was considerable variation in the character and quality of the residua, which, when treated with air, gave varying results.

If the residuum had been heated or cracked during the process of refining, the resulting air-blown asphalt was short, cheesy, greasy, and sometimes even granular in appearance, and unsuitable for any practical use—either in the construction of roads and streets or for the production of industrial asphalts.

If sufficient steam was introduced into the batch still during refining and care was taken to regulate temperatures below the cracking-point, better quality residua were obtained, and, when air-blown, produced much better asphalts and required less blending of natural products.

As most of the early experiments and practical applications of air-blown asphalts were produced from residua made by refining Ohio crude, which contained a high percentage of paraffin, and because the resulting products from the refineries were not uniform, comparatively slow progress was made in commercializing air-blown products, and an unfair trade prejudice developed against them.

It was not until 1908, or until after the discovery of heavier crude oils of an asphaltic base in Illinois and Kansas, that the industry of producing air-blown asphalts became an important factor. These heavier semi-asphaltic oils produced better residua which made much better air-blown asphalts and which, for the first time, produced air-blown asphalts of good quality without the addition or blending of natural asphalts. It was during this period that air-blown asphalts were first used successfully for paving and road work. Shortly after air-blown asphalts were produced from the more highly asphaltic oils of Texas and California.

Table I, made in 1910, is typical of the effect of blowing Illinois residuum, as produced at that time, in a commercial still containing approximately 1,200 gal. of residuum.

The converting kettle in which this was made was equipped with a 2-in. perforated pipe running the full length of the kettle about 1 in. from the bottom. The air was supplied by a low-pressure air compressor. The oil

TABLE I

Properties of Blown Oil

Hours blown	Sp. gr. at 25°C.	Penet. 50 g., 5 s., 0°C.	Penet. 200 g., 1 m., 0°C.	Penet. 50 g., 5 s., 25°C.	Penet. 100 g., 5 s., 25°C.	Penet. 50 g., 5 s., 45°C.	Engler at 100°C.	N.Y.T.L. at 100°C. float test	Flash-point (Cleveland open cup)	Melting-point, cube-method	Fixed carbon	Total bitumen sol. in CS_2	Soluble in 86° Bé. naphtha	Loss at 25°C., 50 g., 5 hr.	Penet. residue from loss
		mm.	mm.	mm.	mm.	mm.	m. s.	m. s.	° F.	° F.	%	%	%	%	mm.
0	0·952	..	..	..	..	..	2 1	0 10	435	..	4·08	99·92	98·74	3·9	..
2	0·954	24·3	..	..	..	..	2 17	0 10	..	..	4·42	..	97·13	3·9	..
4	0·957	19·5	..	..	..	..	2 43	0 11	..	..	5·32	..	94·30	3·7	..
6	0·960	14·0	..	..	..	..	3 37	0 13	..	..	5·87	..	91·94	3·7	..
8	0·964	9·3	..	..	..	..	7 1	0 16	455	..	6·78	..	84·67	3·7	..
10	0·968	5·6	25·0	..	..	..	12 24	0 21	..	92	7·65	..	83·05	3·6	..
12	0·969	3·7	14·5	19·2	34·5	..	24 20	0 38	..	123	8·40	..	76·33	3·5	10·5
14	0·973	2·0	8·5	10·2	16·9	27·1	..	1 50	458	163	8·53	..	70·62	3·0	8·8
16	0·974	1·5	7·0	7·2	10·9	16·0	..	3 0	..	181	9·86	..	69·46	3·3	6·0
18	0·976	1·3	6·0	5·7	8·7	11·7	..	7 55	..	208	10·18	..	67·19	2·9	4·5
20	0·977	1·2	5·1	5·0	7·6	9·6	..	..	462	227	10·36	99·87	66·46	2·9	4·4
22	0·977	0·9	4·7	4·3	6·5	8·1	..	..	..	241	10·53	..	65·56	2·8	4·3
24	0·979	0·9	4·3	3·9	6·0	7·7	..	..	..	246	10·71	..	65·05	2·8	4·0
26	0·980	0·9	4·0	3·3	5·4	7·0	..	..	482	249	10·83	..	64·83	2·8	3·5
28	0·981	0·9	3·6	3·0	5·0	6·2	..	..	..	258	11·05	..	64·15	2·8	3·0
30	0·982	0·7	3·5	2·8	4·7	5·8	..	..	..	265	11·20	..	64·02	2·7	3·1
32	0·983	0·7	3·3	2·7	4·4	5·5	..	..	..	274	11·34	..	63·79	2·3	3·0
34	0·983	0·7	3·2	2·6	4·0	5·1	..	..	498	283	11·44	..	63·53	2·4	2·9
36	0·984	0·7	3·1	2·5	3·8	4·8	..	..	..	289	11·50	..	63·51	2·4	3·0
38	0·985	0·6	2·8	2·2	3·7	4·6	..	..	..	294	11·60	..	63·43	2·4	3·0
40	0·987	0·5	2·3	2·2	3·6	4·5	..	..	517	300	11·60	99·85	63·30	2·3	2·9

TABLE II

Effect of Air-treatment on Blended Oils

	Mexican oil				75% Mexican, 25% Illinois				50% Mexican, 50% Illinois				25% Mexican, 75% Illinois				Illinois oil				
Hours blown	Softening-point, ° F.	Penet. at 77° F.*	Penet. at 32° F.†	Penet. at 115° F.‡	Softening-point, ° F.	Penet. at 77° F.*	Penet. at 32° F.†	Penet. at 115° F.‡	Softening-point, ° F.	Penet. at 77° F.*	Penet. at 32° F.†	Penet. at 115° F.‡	Softening-point, ° F.	Penet. at 77° F.*	Penet. at 32° F.†	Penet. at 115° F.‡	Softening-point, ° F.	Penet. at 77° F.*	Penet. at 32° F.†	Penet. at 115° F.‡	Hours blown
1	118	125	..	..	T.S.§	T.S.§	..	..	T.S.§	..	..	..	T.S.§	..	..	..	T.S.§	..	..	..	1
2	124	116	..	..	T.S.§	T.S.§	..	..	84	T.S.§	..	..	80	T.S.§	..	..	T.S.§	..	..	..	2
3	130	96	..	..	94	220	..	..	96	190	..	..	94	190	..	..	T.S.§	..	..	..	3
4	140	90	..	..	102	190	200	..	108	135	90	170	116	165	..	..	92	260	..	..	4
5	144	75	..	..	108	155	..	..	122	95	..	..	144	100	..	..	123	178	..	..	5
6	146	66	..	..	112	135	..	..	145	78	57	122	162	78	68	126	163	109	70	195	6
7	148	57	22	196	118	115	..	..	166	60	..	..	174	67	..	..	181	72	..	..	7
8	150	48	..	..	126	95	40	230	190	48	..	..	188	53	..	..	208	57	64	90	8
9	152	42	..	..	136	80	..	..	204	37	36	82	204	39	37	75	227	50	..	..	9
10	154	40	..	..	144	70	32	156	216	33	..	..	220	33	..	..	241	47	..	..	10
11	157	37	..	..	150	60	..	..	238	25	..	..	232	29	..	..	249	43	..	..	11
12	159	34	..	..	158	51	..	..	255	19	25	54	240	26	23	50	258	39	25	48	12
13	163	31	..	..	167	46	22	110	268	16	..	..	251	25	..	..	265	33	..	..	13
14	168	27	15	60	175	44	..	..	281	14	..	..	255	23	..	..	274	27	..	..	14
15	178	22	..	..	181	36	..	..	292	13	..	..	267	22	..	..	283	22	..	..	15
16	186	19	..	..	188	31	16	65	304	12	18	28	275	19	20	36	294	18	..	..	16
17	194	17	..	..	194	30	..	..	316	12	..	..	282	17	..	..	318	16	18	23	17
18	202	15	8	38	201	29	..	..	330	11	..	..	290	16	..	..	330	15	..	..	18
19	210	15	..	..	206	28	..	..	345	10	12	16	298	15	..	..	345	14	..	..	19
20	218	13	..	..	216	25	14	33	350	9	..	..	312	14	..	..	362	12	..	..	20
21	232	12	..	..	222	23	..	..	362	8	..	..	321	14	15	20	374	11	..	..	21
22	240	11	..	..	230	21	..	..	368	7	7	8	334	12	..	..	380	10	12	14	22
23	251	10	6	19	238	20	12	30	374	7	..	..	342	12	..	..	..	..	..	..	23
24	264	8	..	..	246	18	..	..	380	6	..	..	350	11	..	..	..	..	..	..	24
25	276	6	..	..	255	16	..	..	384	6	..	..	358	11	10	12	..	..	..	..	25
26	284	5	..	..	261	15	..	..	390	6	7	8	366	10	..	..	..	..	..	..	26
27	298	5	..	..	270	13	..	..	..	..	..	..	371	9	..	..	..	..	..	..	27
28	310	5	..	..	278	11	10	18													28
29	318	5	4	8	288	10	..	..													29
30	326	5	..	..	292	8	..	..													30
31	332	5	3	7	305	7	9	14													31
32	..	..	..	..	315	7	..	..													32

* Penetration at 77° F., 100 g., 5 sec. † Penetration at 32° F., 200 g., 1 min. ‡ Penetration at 115° F., 50 g., 5 sec.

§ 'T.S.' indicates that material is too soft (liquid) to determine its softening-point.

was heated to a temperature of approximately 200° F., at which time the air was introduced into the oil and the temperature increased gradually until it reached a maximum of 425° F. On account of the fact that the treatment of petroleum residuum by air produces an exothermic reaction, the heat created was sufficient to raise the temperature from 300 to 425° F. without any external heat being applied. The slow conversion of the oil as shown in Table I was due principally to the comparatively small amount of air introduced and the poor distribution of this air through the heated mass of oil.

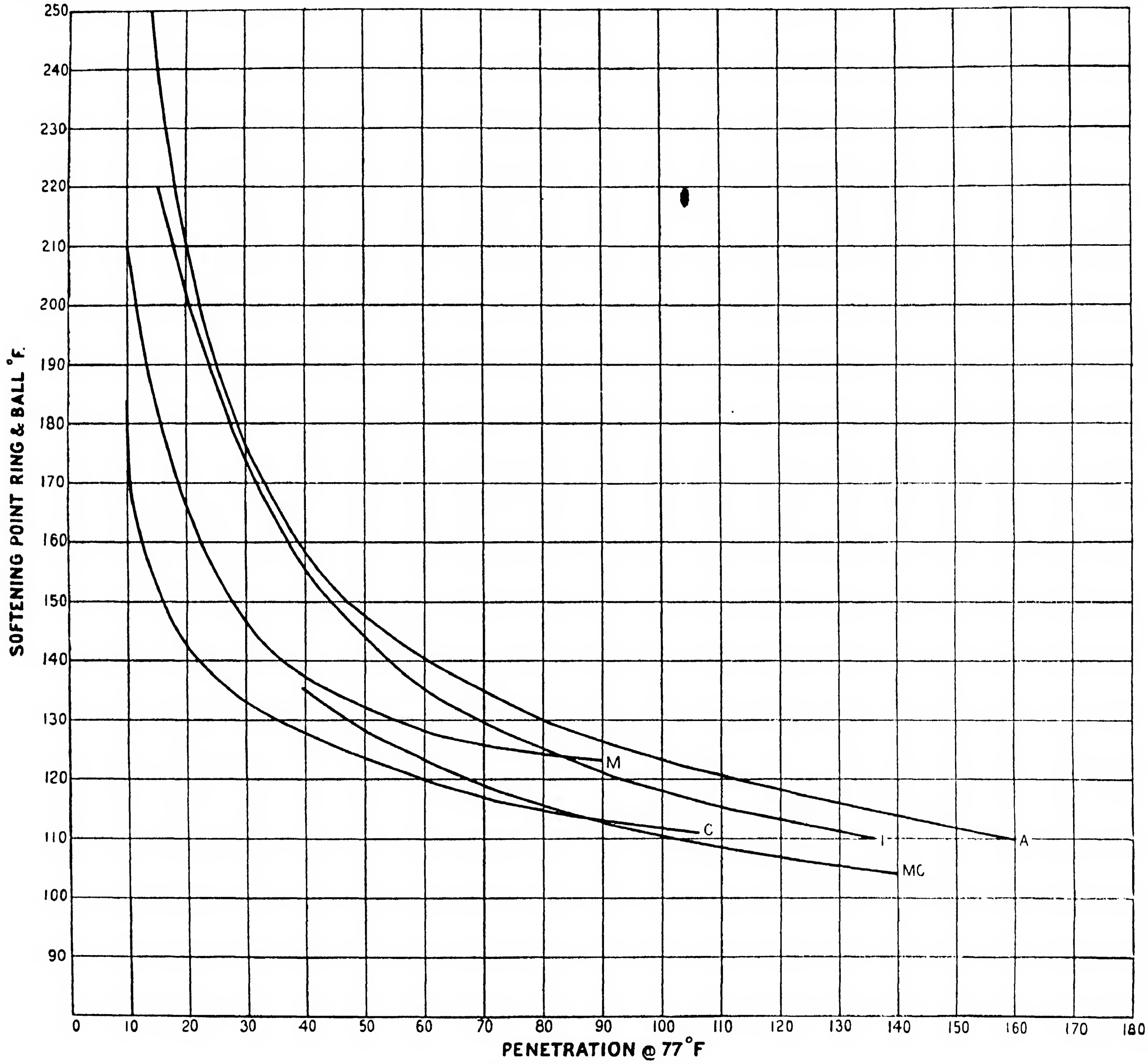


FIG. 1. Blowing curves. Fluxes from various crudes.
A—Arkansas flux. *C*—California flux. *I*—Illinois flux. *M*—Mexican flux. *MC*—Mid-Continent flux.

The asphalts produced, as shown by this table, had a very low susceptibility to temperature changes and good adhesive properties, but they were very low in ductility and required blending with Gilsonite in order to produce satisfactory paving cements.

During the period between 1910 and 1920 considerable progress was made in the development and commercial use of air-blown asphalts. Improved methods of refining produced continually better and more suitable grades of residuum for air treatment. During this period these products were more extensively introduced to the paving, road building, and roofing industries, and their successful use created a rapidly increasing demand.

Due to the successful results obtained from the use of air-blown asphalts in the roofing industry, numerous air-blowing installations were made in roofing plants throughout the country, and, in order to get the most satisfactory results, the blending of residua for air treatment was common practice.

During this period Mexican residuum was used principally as the base material, due largely to the fact that it produced non-staining asphalts. The Mexican oils, however, when blown straight produced products too hard and too susceptible to temperature changes. To overcome these objections, from 10 to 15% of Mid-Continent oils were blended before being air blown.

Table II shows the effect of blending Illinois residua with Mexican in varying proportions as shown. It will be noted from this table that as the blending of the semi-asphaltic Illinois residuum with the pure asphalt Mexican residuum was increased, the susceptibility to temperature changes was decreased and the melting-point substantially raised for the same penetration.

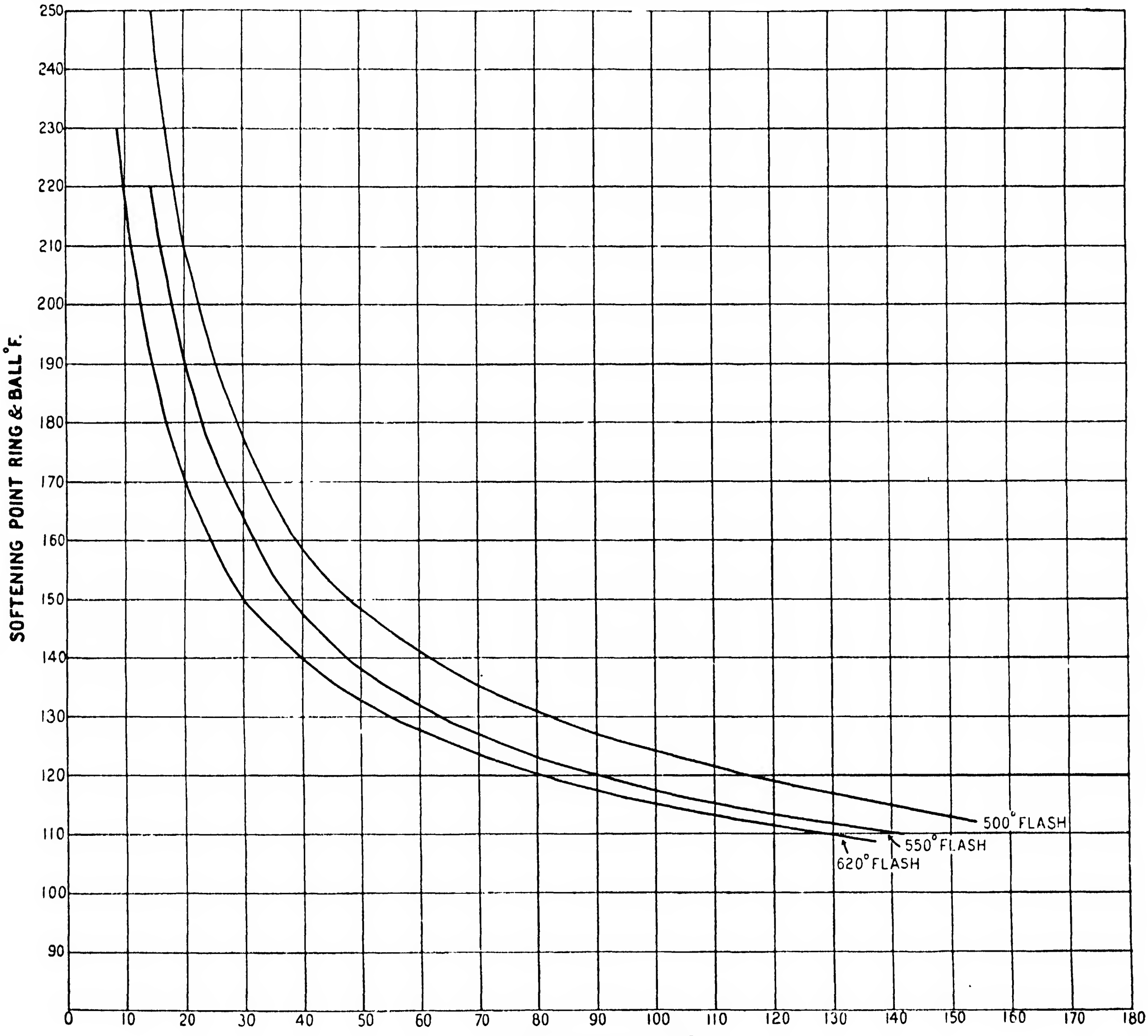


Fig. 2. Blowing curves. Fluxes from same crude.

Since 1920, and up to the present time, revolutionary changes in the refining of petroleum products have taken place, with the resulting changes and progress in the production of air-blown asphalts.

Air-blown asphalts are to-day manufactured from a great many crude oils—practically all crudes containing, by certain processes of refining, some percentage of asphalt. The better grades of asphalt are, however, still being produced from the pure asphalt crudes of Mexico and California and from the small asphaltic oilfields in Texas, Arkansas, Wyoming, Kansas, and Oklahoma. The latter production is not large, and the asphaltic crude is limited to restricted areas and from comparatively shallow production. The quality of the asphalt produced from these fields is, however, comparable to that of the Mexican and Californian oils.

With modern methods of refining, residua can be so refined that different grades can be produced from the same crude, and when air treated will produce asphalts of any desired consistency or specification.

Fig. 1 shows the effect of air on different types and grades of crude oil, while Fig. 2 shows the effect of air-blowing on three different grades of residuum produced from the same crude oil by reducing to different flash-points.

The difference between the 500° F. flash-point residuum shown in Fig. 2, as compared with the 620° F. flash residuum, represents approximately 20% of distillation, which, in this particular case, consisted of heavy lubricating-oil fractions—the 500° F. flash-point residuum representing 70% of the original crude oil, and the 620° F. flash-point residuum representing 50% of the crude oil.

The present practice in the manufacture of asphalt is to reduce the crude oil by means of tube stills and evaporating towers, or vacuum towers, to a predetermined consistency, which may represent the finished product or a residuum to be further air-treated into finished products.

Various types of equipment are used for air-blowing residua—different shapes of stills, different types of blowers, different methods of heat control and fume removal. The most common modern air-blowing still is a cylindrical still having a capacity of from 6,000 to 20,000 gal. The air is supplied from a positive displacement blower operated by an electric motor or steam engine. The blower consists of two impellers rotating in a close-fitting case with each revolution of the blower. The air is introduced into the bottom of the still through perforated pipes—bubbling up through the heated residuum oil to the surface, during which period it has chemically reacted with the heated oil. The effect of a large volume of air passing through the residuum keeps it in a violent state of agitation, and the action produces gases and fumes which require immediate removal from the still.

The quantity of air required varies with the type of residuum being used. Some residua are much more sensitive to air than others and the reaction more violent. As a general rule, it has been found, however, that the most economical conversion takes place by introducing into the residuum from 75 to 150 cu. ft. of air per ton per min.

The use of low-pressure, high-volume blowers, the better distribution of air through the converting kettles, and the high flash-point of residua now being produced have materially reduced the period of blowing and have made it possible greatly to increase the quantity of residuum blown at one time. Asphalts which formerly required from 30 to 40 hr. of blowing are now made in from 5 to 7 hr. The temperatures at which blowing takes place have increased from under 425° F. to between 500 and 600° F. In semi-open stills the maximum blowing temperature should be not more than 25° below the flash-point of the residuum being treated.

Heavy residuum oil appears to have certain characteristics inherited from the crude from which it is produced. The normal characteristics expected from air-blowing may, however, be changed to some extent by the processing method. For instance, introduction of steam into the converting kettles during the process of blowing produces more highly ductile and less staining asphalts than can be obtained without the use of steam. The variation of blowing temperatures in the still may also affect the characteristics—particularly the ductility, there apparently being a range of temperature for each residuum above and below which ductilities of the finished product are reduced.

The addition of foreign substances in the residuum before air-treating—such as resin, rubber, sulphur, pitches, vegetable and animal oils, natural asphalts, and other products—very materially change the character of the finished product.

Those conversant with the art are continually finding numerous small but important details in air treatment that may apply generally to all residua, or only particularly to the residuum under treatment. This is especially true with blended products.

Due to the complex structure of hydrocarbons, it has been impossible so far to determine definitely just what reactions take place during conversion of the oil from a liquid to a semi-solid or solid. It is generally admitted that this is an oxidizing reaction; but in carefully made experiments, little or no water seems to have been formed from the oxygen combining with the hydrogen. Likewise, in the ultimate analysis of products produced, there seems to be no appreciable fixation of oxygen.

During the conversion fumes are given off, varying in amounts and character with different residua. Generally, however, there is no appreciable loss in converting any residuum from a liquid to a semi-solid—the maximum on practically any type of residuum now used being less than 5% in converting an oil softer than 300 penetration to a semi-solid with a softening-point of over 300° F.

In air treatment of residua it is essential that the fumes created during the process be rapidly removed from the convertor. This is accomplished by having several large outlets on the convertor to permit the free passage of fumes or to withdraw them as rapidly as produced by suction fans. Failure to remove these fumes as quickly as created may cause a formation of stalactites in the converting kettles, and the condensation and dropping back of these fumes retards to a considerable degree the period of blowing and changes to some extent the characteristics of the blown product.

Due to the fact that different residua produced from different crudes act differently under air treatment, it is advisable in blowing an unknown residuum to experiment and endeavour to find out the most critical blowing temperatures or range of temperature, and to determine by tests the physical properties of the asphalt produced at varying temperatures.

Present practice requires intimate dispersion of the air throughout the mass of oil, and the period of blowing depends upon the relative amount of air forced through the oil, the distribution of the air throughout the mass, and the temperatures at which the blowing takes place.

During the past few years many devices and methods have been tried for more effective distribution of air and for a unit that will permit continuous production of blown asphalt of any desired grade. Mechanical air mixers are one of several types, all of which, however, have as their main function the obtaining of better air distribution than may be obtained by means of the perforated pipe. By this method air is pumped into a revolving paddle-wheel or is sucked in by venturi pumps, which gives fine dispersion of air globules through the oil and which definitely decreases the blowing time required (Fig. 3).

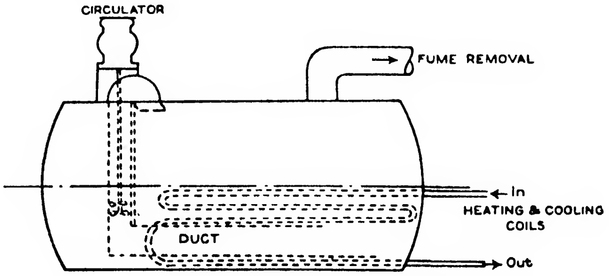


FIG. 3. Accelerated blowing still.

Fig. 4 illustrates a continuous batch-still blowing operation which permits the blowing of different grades of asphalt at the same time, or the continuous production of one grade.

Large producers of air-blown asphalt are now treating large quantities of residuum in large tanks holding from 1,000 to 5,000 bbl., varying in diameter from 5 to 20 ft. and from 10 to 30 ft. in height. It has been found advisable to increase the height rather than the diameter, giving the air globules a longer passage through the heated residuum and increasing the air efficiency. Such installations require the use of large air compressors with sufficient pressure for the air to penetrate easily through the head of oil being treated.

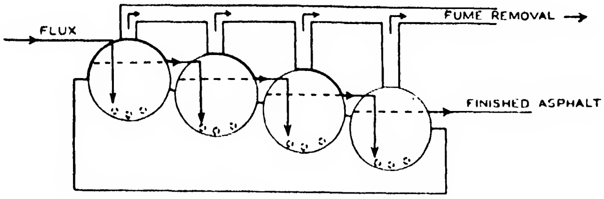


Fig. 4. Continuous batch still.

There is every indication that the new developments for air treatment and the experiments taking place will result in more successful and more economical operations and the production of better blown asphalts. It is quite probable that progress made during the next few years will make present blowing equipment and practice obsolete.

Blown asphalts have proved their merit through years of service and practical tests under all types and varying conditions. They are used almost exclusively in the manufacture of asphalt roofing and shingles; are a most important and essential ingredient of rubber insulating and waterproofing compounds, protective coatings, and paints; and are used to a large extent in the production of battery boxes, battery seal and sewer-joining compounds, fillers and pipe coatings, grave vaults, and floor planks.

There has been perfected and now being used by the U.S. Government large quantities of blown-asphalt reinforced compounds for revetment work along the Mississippi, with similar products in the experimental stage for reclamation and flood control.

Blown asphalts are identified by stability, low susceptibility to temperature changes, weather and water resistance, pliability, and tensile strength, as compared to steam-refined material or asphalt produced from cracking processes.

Further progress and different types of material can be anticipated by more universal blending of residuum oils with other products before air treatment. There are already many of these blends being used for industrial purposes. With the constantly increasing scientific knowledge of blowing and blending, more satisfactory results and a greater variety of products will, no doubt, be developed. There is every indication that in the near future many additional commercial uses will be developed for the consumption and use of air-blown asphalt.

ASPHALTIC BITUMEN EMULSIONS

By F. H. GARNER, Ph.D., F.I.C., M.I.A.E.
Anglo-American Oil Company, Ltd.

ASPHALTIC bitumen emulsions have been developed for use in road construction largely because asphaltic bitumen in this form can be applied to the road surface cold: the viscosity of such emulsions is naturally low, so that no heating whatever, prior to application, is necessary, as is usual with bitumens and cut-backs. The emulsions marketed normally contain from 50 to 65% of bitumen, a small proportion of emulsifier—½ to 1%—the remainder being water.

Patent literature relating to the manufacture of bituminous emulsion is very comprehensive and a summary up to 1928 will be found in *Technisch verwendbare Emulsionen* by Dr. Aladin [1, 1928]. (More recent lists of patents on emulsions are given under reference 1.) The first patent on bituminous emulsions was apparently a German patent of 1886 [6], but it is only in the last 15 years that asphaltic bitumen emulsions have been widely developed for road use. It is not, however, possible to refer in detail to the numerous patents that have been taken out, but the following cover some of the more important developments.

H. A. Mackay, 1922, B.P. 202,021, issued in 1922, describes the manufacture of emulsion in which the emulsifying agent employed was a soap which was formed during the emulsifying process: 2·5–5% of fatty acid, such as oleic acid, is mixed with the molten bitumen and the necessary quantity of caustic alkali added to the water; thus the soap is formed in the process of emulsification by the mixing of the bitumen and the aqueous solution.

In another process, that of J. A. Montgomery, B.P. 254,232, of 1935, a small amount of preformed emulsion is placed in the mixer and the molten bitumen and aqueous solution are introduced into this emulsion, whilst the stirrer is in operation. The preformed emulsion present helps in the emulsification of the bitumen, and smaller quantities of the emulsifier are used than would be required to manufacture emulsion in the absence of the preformed emulsion. In this process, sometimes referred to as the mother liquor process, as soon as one batch of emulsion is completed it is run off, leaving a sufficient quantity inside the mixer for the manufacture of the next batch of which the components are introduced in the same manner as already described.

A very large number of different forms of emulsifying agents have been patented for the manufacture of bitumen emulsions, but the most commonly employed are soaps derived from Swedish liquid rosin, oleic acid, or naphthenic acid. Swedish liquid rosin is a by-product from the manufacture of wood cellulose, and contains in addition to rosin approximately 50% of oleic or similar organic acid. Colloidal clays, such as bentonite, are also used to a considerable extent, and in addition such materials as casein, palmitin, stearin pitch, and a number of fats have been and are being used industrially.

Manufacture of Emulsions

Two principal types of plant used in the manufacture of emulsion are (1) the colloid mill, and (2) the batch mixer. Of these two types the more popular is undoubtedly one or other form of the colloid mill, or homogenizer, although the paddle mixer is still employed in a large number of factories. In the first of these processes the bitumen and aqueous solution are introduced simultaneously into the mill, and dispersion of the bitumen is effected largely by the grinding action of the two faces of the mill. An emulsion is thus produced, and the degree of dispersion depends, to a certain extent, on the speed and clearance between the two faces of the mill. This process is relatively simple to operate, although precautions must be taken to ensure that the proportion of bitumen and aqueous solution fed to the mill is kept constant in order that a uniform grade of emulsion is produced. Such proportioning is normally effected on the pumps feeding the bitumen and aqueous solution to the colloid mill.

The following account briefly describes the process of the manufacture of asphaltic bitumen emulsions, using a colloid mill. The bitumen, which will usually be received in an insulated tank in a molten condition, is pumped into a storage tank where the temperature is adjusted to 110/120° C., and when the soap is to be formed *in situ*, the fatty acid introduced into and mixed with the hot bitumen. A similar storage tank is filled with water containing either the alkali or preformed soap. Both the asphaltic bitumen and aqueous solution may then be pumped direct to the machine in the proportions required in the emulsion or fed to the machine from overhead tanks. The most convenient arrangement is to employ synchronized pumps, adjusted to give the right proportions, which are coupled to the motor which drives the colloid mill. The various types of homogenizer and colloid mill differ in details of construction, but, in general, all have one feature in common. The materials to be emulsified are fed into a central space between the rotor and stator and are then forced to the circumference by the centrifugal force developed by the rotation of the rotor and finally passed through a small gap between the faces of the rotor and stator. Machines employed for the manufacture of bitumen emulsions on a commercial scale have rotors usually 12 to 14 in. diameter and are designed to operate at speeds up to 10,000 r.p.m. Clearance between the rotor and stator is adjustable and in most machines varies from two thousandths of an inch upwards. The throughput varies naturally with the type of machine, but figures of 1,000 to 2,000 gal. of emulsion per hour are quite common. Some of the more important machines used for this work are the following: the 'Premier' Colloid Mill; the 'Hurrell' Homogenizer; and the Hatt-Dussek Homogenizer [5].

In the manufacture of emulsions by Paddle Mixer processes a number of modifications of the method of procedure are used, and there is probably a greater variation in the type of plant employed than is the case where colloid mills are employed. Essentially, however, the plant consists of a vertical cylindrical tank furnished with a propeller which rotates normally at low speeds, although the actual speeds employed may vary from 50 r.p.m. to 1,000 r.p.m.

Emulsification may be effected either by measuring the quantity of bitumen into the tank and then gradually adding the requisite quantity of aqueous phase, or the bitumen may be added to the aqueous phase contained in the mixer. Batch mixing may be made to operate practically continuously by the installation of suitable equipment. In such a plant the bitumen may be contained in an overhead tank, steam heated, and maintained at the desired temperature, and so arranged, by means of a float control, that an exact quantity of bitumen from this tank can be discharged mechanically into the mixing tank. The aqueous solution containing the soap is made up in large quantities, and fed to a similar tank with mechanical control for the discharge of the aqueous solution into the mixer, at a predetermined rate during the process of emulsification.

In both types of plant the whole operation can be mechanically controlled and manual operation is very largely eliminated. It will be seen that in the case of emulsions formed by the use of soap the following alternatives are possible. The fatty acid or its equivalent may be added to the bitumen; the alkali may be added to the water; or soap may be added to the water; or again, part of the organic acid may be added to the bitumen and the aqueous solution may contain part of the soap required in the finished emulsion as well as the alkali. Variation of these details of operation may produce considerable variations in the quality of the emulsion produced, and, on the whole, the batch process may probably be used to vary the type of emulsion produced more easily than the colloid mill. A further point of interest is that in the colloid mill the time during which the bitumen and aqueous solution are in contact is relatively small, so that in some instances the batch mixer may produce emulsions of finer dispersion than are obtained with the same ingredients in the colloid mill.

In general, however, where the bitumen available is of satisfactory character, the colloid mill is the easier to operate and can be made to produce satisfactory emulsions of uniform quality with relatively little control.

Properties and Manufacture of Bitumens

The type of crude petroleum which can be used in the manufacture of asphaltic bitumen for road purposes is distinctly limited, and in general can be said to be limited to a relatively small number of fields.

In considering asphaltic bitumen from the point of view of the manufacturer of emulsions two special factors have to be taken into account, namely, the ease of emulsification and the production of emulsions of satisfactory storage stability. Whilst a considerable amount of attention has been devoted in the course of the last few years to the essential qualities of the bitumen necessary to enable emulsification to be readily effected, fundamental knowledge on this subject is limited. Bitumens from certain crude oils emulsify readily, whereas with bitumens from other fields in the same neighbourhood it is a matter of some difficulty to obtain satisfactory emulsions. Apart, however, from the crude oil used in the manufacture of bitumens, a matter of great importance is the careful control of the conditions of manufacture of the bitumen.

In the more modern type of plant, pipe stills and one or more flash towers are used for the manufacture of asphaltic bitumen instead of the older type of batch still, and the main advantage of the flash method is that the bitumen in process of manufacture is exposed to high temperatures for a short time and thus decomposition of the asphalt which might affect its emulsifying qualities is avoided.

Properties of Asphaltic Bitumen Emulsions and their Relation to Practice.

The essential properties of bituminous emulsions from the point of view of their behaviour when used for surface dressing or grouting have been found to correlate with the following six tests which have been adopted (British Standard Specification no. 434, 1935).

1. **Water Content.** This is determined by distillation with a suitable solvent in a modification of the Dean and Stark apparatus.

2. **Residue on Sieving.** A test for the presence of large particles in the bituminous emulsions, which is of importance in so far as their suitability for spraying is concerned. A definite quantity of emulsion is passed through a fine mesh sieve, B.S. mesh 100, and the amount of material left on the sieve determined. This particular test is of importance mainly where machines are used for the spraying of the emulsion in which the emulsion has to pass through a series of fine holes, which would be blocked up if any considerable proportion of large particles were present.

3. **Test for Storage Stability.** One of the most important properties of the bituminous emulsions is their stability on storage. Reference should be made to the confusion which has arisen in time past between stability on storage and stability on the road or breakdown, and it was therefore recommended by the Technical Committee of the Road Emulsion and Cold Bituminous Roads Association, which has been responsible for much research work into the properties of bituminous emulsions, that the word 'Lability' be used as a method of distinguishing the latter property. Thus stability on storage indicates the behaviour of emulsions in so far as settling is concerned, i.e. the resistance to separation of the emulsion to its constituent parts over varying periods of time, whereas lability is concerned with the rate of breaking of emulsion on the road. No satisfactory test has yet been standardized which enables the stability of the emulsion in storage over a period of 3 months or so to be reproduced by means of laboratory apparatus in the course of a few hours or a few days. A method has, however, been adopted in the B.S. Specification 434, 1935, which effects a classification of emulsions by means of a short-period stability test (Coagulation of Binder) in which a sample of previously sieved emulsion is placed in a 100-ml. stoppered glass cylinder for 7 days. The emulsion is then examined by passing again through a sieve in order to determine the proportion of the binder which has coagulated. For the determination of stability of emulsions on storage over a long period (Stability in Bulk) the only satisfactory method is to store a barrel of the emulsion of 30–40 gal. capacity over a period of 3 months, and then determine the percentage of water present in a sample of the sieved emulsion. The increase in water content after storage enables the proportion of bitumen which has been coagulated on storage to be determined.

4. **Behaviour in Cold Weather.** Owing to the content of water in asphaltic bitumen emulsions it will be appreciated that solidification occurs when emulsions are cooled to temperatures of much below 0° C. Emulsions can be prepared by the use of special emulsifiers which will withstand relatively low temperatures, but in general such emulsifiers decrease the lability or rate of 'break' of the emulsion to such an extent that sufficiently rapid breakdown may not take place on the road. In the test adopted the bituminous emulsion is exposed to a temperature of −3 to −4° C.

under carefully regulated conditions for 30 min. and the coagulated bitumen determined by sieving after the emulsion has warmed to room temperature. (Test for coagulation of emulsions at low temperatures.)

5. **Viscosity.** A very important property of emulsions is that of viscosity, since, as already mentioned, it is primarily on account of low viscosity of these materials that they have been developed in competition with other materials which require heating prior to use. The viscosity of the emulsion must be controlled within fairly narrow limits, since the viscosity must not be so high that it cannot be sprayed or applied satisfactorily. Hence the upper limit of the viscosity will depend, to some extent, on the type of machine and pressures employed for application of the emulsion to the road surface. On the other hand, if the emulsion is too fluid, it may run off the road surface before sufficient time has elapsed for the emulsion to break. For surface dressing higher viscosity emulsions can be used than for grouting purposes, for which it is essential that the emulsion should penetrate easily into the compacted road material.

The instrument which has been adopted by the British Standard specification for determination of the viscosity of emulsions is the Engler viscometer, as this instrument has been found to be more suitable than either the Redwood or Saybolt.

6. **Lability, or Breakdown, of Emulsions on the Road.** A considerable amount of work during the last few years has been directed towards investigations on the mechanism of breaking of emulsions on the road, and a number of methods of test developed. The four factors which may contribute to the breakdown of emulsions are:

(*a*) Evaporation of the water present in the emulsion with the result that a certain point is reached where the bitumen particles coalesce and the emulsion is broken.
(*b*) Chemical reaction between the emulsifier and soluble salts assumed to be present in the aggregate.
(*c*) Adsorption of emulsifier on the stone or road surface.
(*d*) Loss of water by capillary forces.

In the British Standard specification for Surface Dressing and Penetration Emulsions, British Standard Specification no. 434 (1935), the Lability Test has been adopted for determining the rate of break of emulsions, and this test is based on the assumption that with these types of emulsion evaporation of the water present in the emulsion, combined with the mechanical action of the roller on the emulsion, are primary factors in the irreversible breaking of the emulsion. In this test 1 g. of the emulsion is placed in a porcelain crucible and concentrated under a gentle current of air at a temperature of 18–20° C., the emulsion being stirred during this concentration by means of a small glass rod. The coagulation point is determined by removing a drop of the emulsion from the crucible to a glass plate from time to time and mixing the emulsion with a drop of water. When the emulsion is broken, a substantial portion of the coagulated binder will be visible on the plate or glass rod. This test requires careful manipulation to ensure satisfactory results, and full details are given in the British Standard Specification no. 434 referred to above.

The water content of the residual material is determined and unstable emulsions, suitable for surface dressing and grouting, should give 13·25% water content.

The above series of tests was considered at the Munich Meeting of the International Association of Road Congresses in September 1934, and referred to a Committee for adoption. The report of this Committee is given in the *Bulletin of Road Congresses* for 1935, no. 102, p. 383. It was decided to adopt the tests 1–5 mentioned above, and the value of test no. 6 was agreed and also that the large number of concordant results justified the anticipation of its proving satisfactory, but a sub-committee was appointed to carry out further experiments and to submit final details of this test.

The American Society for Testing Materials has adopted the following tests for emulsified asphalts [2, 1935]:

(1) Viscosity, by determination of the Saybolt 'Furol' viscosity at 25° C.
(2) Distillation test.
(3) Water determination by the Dean and Stark method.
(4) Five days' settling test. 500 c.c. of emulsion are stored in glass cylinders for 5 days, and the asphalt content of the top and bottom samples determined.
(5) Demulsibility by means of calcium chloride solution. The emulsion is treated with a 0·02% N. calcium chloride solution for mixing type emulsions, with continuous stirring at 25° C.±0·5° C. The emulsion is then sieved through a no. 14 U.S. standard sieve and washed. The weight of asphalt which has been coagulated is determined and expressed as 'percentage demulsibility'.
(6) Sieve Test. The emulsion is passed through a no. 20 U.S. standard sieve and washed with 2% sodium oleate solution. The weight of material retained on the sieve is determined after drying at 105° C. for 2 hr.
(7) Miscibility with water. (This test is not applicable to the quick-setting type of emulsions.) 50 ml. of emulsion are gradually added to 150 ml. of distilled water, and after standing for 2 hr. any appreciable coagulation is noted.
(8) Coating Test. Washed, dried, and graded stone (hard limestone, trap rock, or other type) is coated with emulsion and stored. A record is made whether appreciable coagulation has occurred of the asphalt from the water of the emulsion, and whether the stone is uniformly and thoroughly coated with the emulsion.
(9) Freezing Test. The emulsion is cooled to 0° F. for 12 consecutive hours and, after thawing and freezing for three periods of 12 hr., the emulsion is examined and reported as homogeneous or broken.

Specifications for emulsified asphalt issued by the American Society for Testing Materials are D. 397–401/34T, which describes Coarse Aggregate Mix, Heavy Premix—both Summer and Winter grade—and also quick-setting emulsions for penetration and surface treatment.

The German specifications for bitumen and tar emulsions, DIN. 1,995 (1934), p. 8, describe tests for emulsions as follows: uniformity, water content, ash content, storage stability, behaviour under frost, adhesivity, and rate of break, together with tests on the bitumen.

Breaking of Emulsions on the Road

During the last 4 or 5 years much research has been concentrated on the mechanism of the breaking of bituminous emulsions under similar conditions to those found in practice. The Lability Test, already described, has been found satisfactory to correlate with the behaviour on the road in the case of surface-dressing emulsions, but in America the Myers test, using calcium chloride solution, has been adopted by the American Society for Testing Materials. A fairly complete summary of the work carried out in various countries will be found in the *Proceedings of the World Petroleum Congress* for 1933 (vol. ii, pp. 629–92), and in particular the work of Weber and Bechler is described in a paper by Weber, and the Myers Test in papers by Kirschbraun and McKesson. McKesson [12, 1931] developed a stone-coating test in 1928, in which clean gravel was immersed in asphalt emulsion and after drying for 30 min. the increased weight due to the asphalt deposited on the gravel was determined: this test was proposed as a measure of the rate of break of the emulsion. McKesson emphasized the importance of temperature, humidity, and the type of gravel employed, but no indication is given of the wide variations which may occur with gravel of different origins. Weber and Bechler [17, 1932] used a similar test, but with much smaller quantities of emulsion and stone, and reached the conclusion that soap-stabilized emulsions break owing to adsorption by the stone of soap and free alkali: other emulsions are said to break down by evaporation of the water. Kell [10, 1933] showed that it was difficult to obtain concordant results with this method, and concluded that whilst this method is useful for research it is not entirely satisfactory for the evaluation of either the stone or the emulsion. Certain modifications of the method were suggested by Weber [16, 1933] who stated that the method is essentially practical rather than an exact analytical method.

The factors governing the adhesion of bituminous binder to stone have been discussed in recent literature by Riedel and Weber [15, 1933] which has thrown some light on the breakdown of emulsions on stone: in general, basic aggregates give satisfactory adhesion, whereas with acidic aggregates, such as quartz, it is a matter of considerable difficulty to secure satisfactory adhesion of the bitumen to the stone. The Riedel test for determining the adhesivity of bitumen [14, 1934] to stone has been criticized on the ground of lack of correlation with road practice [13, 1935], and somewhat similar criticisms have been made of the McKesson, of the Myers [11, 1933], and the lability [8, 1935] tests for determining rate of break of emulsions.

Blott and Osborn [3, 1934] point out that, as soon as the emulsion comes into contact with the stone, coagulation occurs due directly to the chemical action or adsorption, as pointed out by Weber and Bechler. The film of bitumen varies in thickness according to the type of stone or emulsion, but in any case is quite thin, since the mere coating of the stone with bitumen must eliminate to a great extent any specific activity of the stone. Furthermore, the stone, although coated with bitumen, is separated by unbroken emulsion, and the further coagulation which is essential for the stone to be held in position on the road can then only occur as a result of concentration of the emulsion by evaporation and not by chemical action. For these reasons the essential basis of the lability test appears to be quite sound.

Stable Emulsions

Asphaltic bitumen emulsions for road-mix work or for admixture with earth must possess a greater stability to breakdown than emulsions for surface dressing or grouting. Such emulsions usually contain special emulsifying agents, although greater proportions of the usual emulsifying agents are also employed. With finer aggregates, or with aggregates containing a larger proportion of 'fines', more stable emulsions are required than those used with coarser aggregates. The rate of break of such emulsions is relatively slow, and it is considered that for this purpose a method of test is necessary which depends on the admixture of the emulsion with a standard active material: with this type of emulsion evaporation is not the most important factor, and consequently the lability test, while satisfactory for emulsions for surface dressing and grouting, is not suitable for stable and semi-stable emulsions. The use of stable emulsions for admixture with fine aggregates or earth requires careful investigation of the most suitable conditions, and these vary with each different aggregate.

Asphaltic bitumen emulsions have been employed for a wide variety of other uses than road purposes, especially in the direction of waterproofing. Such applications of emulsions are the manufacture of waterproof paper for use as packing material for cements or chemicals, or for the manufacture of corrugated cardboard [9, 1935]; other applications are as binder—as, for example, for asbestos for soundproofing—or admixture with cement and sand as flooring material for buildings or tennis courts [7, 1933].

The British Standards Institution has issued specifications for Single Coat and Two Coat Asphalt, Cold Process, which include specifications for emulsion. The tests prescribed for emulsion for this type of asphalt include a stability test based on admixture of the emulsion and stone, water content, initial sieve test, while the maximum proportion of emulsifying agent which may be used is specified [4, 1933].

REFERENCES

1. Aladin. *Technisch verwendbare Emulsionen* (Berlin, 1928). See also Leemans, *Chem. Weekblad*, **26**, 2 (1929), 1, and Van der Werth, *Asphalt u. Teer*, **36**, 383 (1936).
2. A.S.T.M. Specifications D. 397–401/34 T. *Proc. A.S.T.M.* **35**, 923 (1935).
3. Blott, J. F. T., and Osborn, A. *Highways and Bridges*, **1** (12), 12–13 (1934).
4. British Standard Specifications 510 and 511 (1933).
5. See Clayton, W., *The Theory of Emulsions*, 325 seq., for description of Colloid Mills.
6. G.P. 40,020 (1886). Deutsche Asphalt A.-G.
7. Fain, J. M., and Hixson, A. W. *Chem. Met. Eng.* **40**, 180 (1933).
8. Geissler, D. W., and Kleinert, H. *Asphalt u. Teer*, **35**, 1019 and 1038 (1935).
9. Hoyer, F. *Asphalt u. Teer*, **35**, 591, 613 (1935).
10. Kell. *Bitumen*. **3**, 11 (1933).
11. Klinkmann, G. H. *Asphalt u. Teer*, **33**, 842, 873, 893 (1933).
12. McKesson, C. L. *Proc. A.S.T.M.* **31** (Part 2), 841 (1931).
13. Nussell, H., and Neumann, E. *Bitumen*, **6**, 125 (1935).
14. Riedel, W. *Asphalt u. Teer*, **34**, 209, 429, 487, 924, 941, 961, and 979 (1934).
15. Riedel, W., and Weber, H. *Asphalt u. Teer*, **33**, 677, 693, 713, 729, 749, 793, and 810 (1933).
16. Weber, H. *Asphalt u. Teer*, **33**, 520 (1933).
17. Weber, H., and Bechler. *Asphalt u. Teer*, **32**, 45, 69, 95, 109, 129, 149, and 173 (1932).

SELECTED BIBLIOGRAPHY

Garner, Gabriel, and Prentice. *Modern Road Emulsions.*

Wilkinson and Forty. *Bituminous Emulsions for use in Road Works.*

NATIVE ASPHALTS AND BITUMENS

By J. S. MILLER, Jr., A.I.C.E.

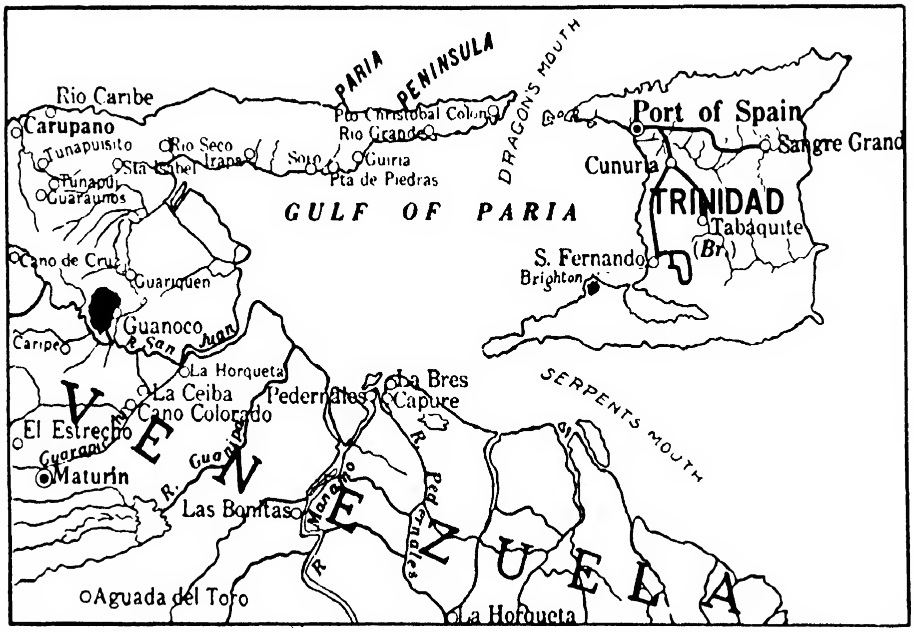
Chemical Engineer, Barber Asphalt Company

Introduction

THE terms asphalt and bitumen are of ancient origin and have been applied interchangeably from the earliest times to several types of bituminous substances that were found in nature, and frequently applied to some useful purpose.

Historical records of the occurrence and practical use of these substances extend back as far as 3000 to 2500 B.C., and archaeologists have identified some deposits, from the skeletons of animals excavated from them, as antedating the pleistocene or glacial period which terminated about 25,000 years ago.

That form of native bitumen which is distinctly recognized as petroleum (liquid bitumen) has been dealt with elsewhere in this publication, hence this section will be devoted to the consideration of only the more solid types, deposits of which are widely distributed geographically on or near the surface of the earth and are generally conceded to have been derived through natural causes from lighter hydrocarbons of various types.



Relative geographical location of Island of Trinidad, B.W.I., and Venezuela, South America, where Trinidad Asphalt Lake (Brighton) and Bermudez Asphalt Lake (Guanoco) respectively are situated.

No attempt has been made here to record all of the known deposits of native asphalts and bitumens. Many have been described in detail elsewhere, and but relatively few of them are of commercial importance at this time. The ancients employed native asphalt and bitumen for such practical uses as mortar for joining masonry and brick; as waterproof coatings for tunnels and aqueducts; as a cement in road-building; and asphalt from Persia, the Dead Sea, Greece, and Mesopotamia was then an article of commerce and sometimes one of the spoils of war. While asphalt is still produced from deposits in Albania and Persia, mentioned by the ancients, the chief sources of supply of native asphalts and bitumens of commercial importance in most recent times are as follows:

West Indies:	Cuban	Discovered	1535
	Trinidad	,,	1595
Europe:	Val de Travers, Switzerland	,,	1712
	Limmer, Germany	,,	1712
	Seyssel, France	,,	1797
	Ragusa, Italy	,,	Early Roman Empire
N. America:	Grahamite, U.S.A.	,,	1863
	Gilsonite, ,,	,,	1885
	Wurtzilite, ,,	,,	1889
S. America:	Bermudez, Venezuela	,,	prior to 1883

Various schemes have been proposed by different authorities for the classification of bituminous substances in order to show the relation of asphalts and bitumens to other members of this general group. One of the more recent and most acceptable of such schemes is that proposed by Abraham [2, 1929] and a grouping of the asphalts and bitumens covered in this section has been arranged as follows, according to this proposal.

Classification of Native Bitumens

1. Petroleums—liquids—viscous liquids.
2. Native asphalts—solid or semi-solid.
   - A. Pure or nearly pure.
     Bermudez Lake asphalt.
   - B. Associated with mineral matter.
     - (*a*) Trinidad Lake asphalt.
     - (*b*) Iraq, Boeton, and Selenitza.
     - (*c*) Rock asphalts—European and American.

3. Asphaltites—hard.
    A. Pure or nearly pure.
        (*a*) Gilsonite.
        (*b*) Grahamite.
        (*c*) Glance pitch—Manjak.

Some bituminous substances of collateral interest but which are of a distinctly different character and cannot properly be included in the above classification are Elaterite, Wurtzilite, Albertite, and Impsonite. These are asphaltic pyrobitumens of which Wurtzilite is of chief interest industrially as it depolymerizes upon heating, becoming fusible and soluble, whereas it is originally quite the reverse.

Bermudez Lake Asphalt

The Bermudez Pitch Lake is situated about 11 miles above the confluence of the San Juan and Guanoco Rivers, 25 miles west of the Gulf of Paria in the north-eastern part of Venezuela. It is near the town of Guanoco in the district of Venitez, State of Sucre. The lake is connected with the loading jetty at Guanoco by a narrow-gauge railroad extending about 8 miles through a swamp. The so-called Pitch Lake is situated between the edge of the swamp and the foot-hill in what might be termed a savannah. It is an irregular-shaped surface of about 900 acres with a width about 1½ miles north and south and about 1 mile east and west, covered more or less with vegetation. The level of the surface of the lake does not vary more than 2 ft. and is largely the same as that of the surrounding swamps. In the rainy season it is mostly flooded and at all times is very wet.

At different points there is a depth of about 7 ft. of asphalt, but the average depth of the lake is probably not more than 4 ft. Gas is given off in considerable quantities and, although the asphalt is too soft to entangle and hold the gas permanently, some portions have a honeycombed structure. The surface of the lake is hard enough to walk upon and the asphalt is dug out by hand labour, moved to tide water by rail, and loaded in bulk into ocean-going ships at Guanoco.

The deposit of Bermudez asphalt appears to owe its existence to an exudation of a large quantity of soft asphalt charged with gas, which has spread over a great area and hardened by spontaneous evaporation in the tropical sun. It varies in hardness and, while not an emulsion, the asphalt is wetted by surface water and mingled with small amounts of vegetable and mineral matter.

The crude Bermudez Lake asphalt has the following average composition:

	%
Water and gas volatilized at 100° C.	30·00
Soluble in carbon disulphide	64·39
Mineral matter on ignition	2·08
Non-mineral matter insoluble	3·53
	100·00

Weight per cubic foot, average 65 lb.

Crude Bermudez Lake asphalt is transported in bulk to the United States in cargo vessels built or selected especially for this trade on account of the difficulties in navigating the shallow and narrow water ways leading to the shipping-point at Guanoco.

This crude asphalt is soft enough to be dug from the holds of vessels or from storage with specially constructed clam-shell buckets. It is steam-refined in the open kettles and by the same method of treatment as described later under steam-refined Trinidad Lake asphalt.

As put in slack barrels, the average weight per package is 320 lb. gross and 300 lb. net.

Steam-refined Bermudez Lake asphalt has been examined by several investigators, and its chemical and physical characteristics as reported in detail by Richardson and Abraham are as follows:

TABLE I

Refined Bermudez Asphalt [10]

Test number	44,412	67,753
Year	1900	1903
Physical properties		
Specific gravity, 78° F./78° F., original substance, dry	1·0823	1·0575
Colour of powder or streak	Black	Black
Lustre	Bright	Bright
Structure	Uniform	Uniform
Fracture	Semi-conchoidal	Semi-conchoidal
Hardness, original substance	Soft	Soft
Odour	Asphaltic	Asphaltic
Softens	170° F.	160° F.
Flows	180° F.	170° F.
Penetration at 78° F.	22	26
Chemical properties		
Dry substance:		
Loss, 325° F., 7 hr.	3·0%	4·4%
Character of residue	Smooth	Smooth
Loss, 400° F., 7 hr. (fresh sample)	8·2%	9·5%
Character of residue	Wrinkled	Shrunken
Bitumen soluble in CS_2, air temperature	95·0%	96·0%
Inorganic or mineral matter	2·5%	2·0%
Difference	2·5%	2·0%
	100·0%	100·0%
Malthenes:		
Bitumen soluble in 88° naphtha, air temperature	62·2%	69·1%
This is per cent. of total bitumen	65·4	71·9
Per cent. of soluble bitumen removed by sulphuric acid	62·4	67·4
Per cent. of total bitumen as saturated hydrocarbons	24·4	23·4
Bitumen soluble in 62° naphtha	69·2%	75·9%
This is per cent. of total bitumen	72·8	79·0
Carbenes:		
Per cent. bitumen insoluble in carbon tetrachloride, air temperature	0·1	1·1
Bitumen yields on ignition:		
Fixed carbon	13·4%	14·0
Sulphur	4·0%	..

TABLE II

Refined Bermudez Lake Asphalt [1]

Fracture	Conchoidal
Lustre	Very bright
Streak	Black
Specific gravity at 77° F.	1·06–1·085
Hardness on Moh's scale	Less than 1
Penetration at 115° F.	60
„ 77° F.	20–30
„ 32° F.	3
Consistency at 115° F.	7·7
„ 77° F.	22·7
„ 32° F.	93·8
Susceptibility factor	62·5
Ductility at 115° F.	14·5
„ 77° F.	11
„ 32° F.	0
Tensile strength at 115° F.	0·60
„ „ 77° F.	3·45
„ „ 32° F.	10·5
Fusing-point (K. and S. method)	130–140° F.
„ (R. and B. method)	145–160° F.

TABLE II (*cont.*)

Volatile matter, 325° F., 5 hr.	3·0–6·0%
„ „ 500° F., 5 hr.	8·0–10·0%
Fixed carbon	12·9–14·0%
Solubility in carbon disulphide	92–97%
Non-mineral matter insoluble	1·5–4·0%
Free mineral matter	1·5–6·5%
Carbenes	0·0–1·0%
Solubility in 88° petroleum naphtha	60–75%
Carbon	82·88%
Hydrogen	10·79%
Sulphur	5·87%
Nitrogen	0·75%
Total	100·29%
Solid paraffines	0·0%
Saturated hydrocarbons	23·25%
Saponification value	28·0%
Free asphaltous acids	3·5%
Asphaltenes	35·3%
Asphaltous anhydrides	2·0%
Asphaltic resins	14·4%
Oily constituents	39·6%

A recent analysis of Refined Bermudez Lake asphalt is recorded in Table III:

TABLE III

Refined Bermudez Lake Asphalt

Test number	74,619
Year	1931
Specific gravity at 60° F. (15·5° C.)	1·0757
Colour of powder or streak	Black
Lustre	Bright
Structure	Uniform
Fracture	Semi-conchoidal
Hardness	Soft
Odour	Asphaltic
Softening point (Ring and Ball method)	139° F. (59·5° C.)
Consistency:	
Penetration at 32° F. (0° C.), 200 g., 60 sec.	4
„ 32° F. (0° C.), 100 g., 5 sec.	2
„ 77° F. (25° C.), 100 g., 5 sec.	20
„ 100° F. (38° C.), 100 g., 5 sec.	92
„ 115° F. (46° C.), 50 g., 5 sec.	122
Ductility at 77° F. (25° C.), 5 cm. per min.	40 cm.
Flash-point (Cleveland open cup)	375° F. (190·5° C.)
Bitumen (soluble in CS_2)	95·5%
Mineral matter	2·3%
Difference	3·2%
Per cent. bitumen soluble in CCl_4	100%
„ „ „ 86° naphtha	73·1%
„ „ „ ethyl ether	81·9%
Fixed carbon (ash-free)	13·2%
Paraffin scale (Holde method)	trace
Sulphur	4·0%
Loss 50 g., 5 hr., 325° F. (163° C.)	1·3%
Residue: penetration at 77° F. (25° C.), 100 g., 5 sec.	16
Residue: ductility at 77° F. (25° C.), 5 cm. per min.	15 cm.
Viscosity furol at 300° F. (149° C.)	220 sec.
„ „ 350° F. (176·5° C.)	60 „
„ „ 400° F. (204·5° C.)	27 „

As is noted in Tables I, II, and III, the refined asphalt is fairly hard (penetration of about 20) and is soluble to the extent of about 95% in carbon disulphide. It is miscible with petroleum residue in all proportions and is usually softened to the degree desired for paving and other purposes by blending it at a temperature of about 300° F. with liquid petroleum residuum. Such blended products are known as asphalt cements, Bermudez Lake asphalt cements, or fluxed Native Asphalts. Typical analyses, taken from data recently acquired, are given in Table IV:

TABLE IV

Bermudez Lake Asphalt Cements

(The liquid petroleum flux used was produced from an asphaltic base crude.)

	25 pen.	*50 pen.*	*80 pen.*
Specific gravity at 60° F. (15·5° C.)	1·074	1·064	1·056
Softening-point (Ring and Ball)	138° F. (59° C.)	126° F. (52° C.)	117° F. (47° C.)
Penetration at 32° F. (0° C.), 200 g., 60 sec.	6	12	19
Penetration at 32° F. (0° C.), 100 g., 5 sec.	2·5	3·5	5·5
Penetration at 77° F. (25° C.), 100 g., 5 sec.	25	50	80
Penetration at 100° F. (38° C.), 100 g., 5 sec.	110	197	Too soft
Penetration at 115° F. (46° C.), 50 g., 5 sec.	146	262	Too soft
Ductility at 77° F. (25° C.), 5 cm. per min. pull	43 cm.	66 cm.	73 cm.
Flash-point (Cleveland open cup)	375° F. (190·5° C.)	380° F. (193·5° C.)	390° F. (199° C.)
Fire-point (Cleveland open cup)	430° F. (221° C.)	440° F. (226·5° C.)	455° F. (235° C.)
Flash-point (Pensky Martin closed cup)	310° F. (154·5° C.)	315° F. (157° C.)	325° F. (163° C.)
Bitumen soluble in CS_2	96·1%	96·7%	97·0%
Mineral matter	2·3%	1·8%	1·6%
Difference	1·6%	1·5%	1·4%
Per cent. bitumen soluble in CCl_4	99·8	99·8	99·9
Per cent. bitumen soluble in 86° naphtha	73·5	75·5	77·0
Per cent. bitumen soluble in ethyl ether	82·2	83·5	84·2
Fixed carbon (ash-free)	13·0%	12·3%	11·8%
Paraffin scale (Holde method)	0·15%	0·21%	0·25%
Sulphur	4·0%	3·75%	3·60%
Loss 50 g., 5 hr., 325° F. (163° C.)	1·22%	1·15%	1·12%
Residue: penetration at 77° F. (25° C.), 100 g., 5 sec.	19	38	60
Furol viscosity at 300° F. (149° C.)	195 sec.	135 sec.	98 sec.
Furol viscosity at 350° F. (176·5° C.)	56 sec.	42 sec.	32 sec.
Furol viscosity at 400° F. (204·5° C.)	26 sec.	22 sec.	17 sec.

Bermudez Lake Asphalt—Uses.

The Bermudez Lake asphalt of commerce has been used principally in the construction of asphalt streets and roads, and for waterproofing, and has been exploited for such use since 1891.

All types of hot mixed asphalt pavements, sheet asphalt and asphaltic concrete, as well as surface coating and penetration macadam, have been constructed with this asphalt. It has also been used extensively in the manufacture of emulsified asphalt and cut-back asphalt for roads; in roofing, and in waterproofing.

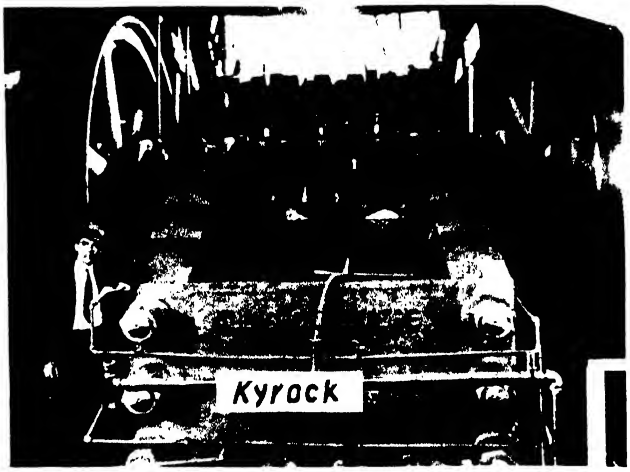
Trinidad Lake Asphalt

One of the largest deposits of native asphalt in the world occurs on the Island of Trinidad, B.W.I., off the north-east coast of South America, situated a short distance from Venezuela, and separated from the mainland by the Gulf of Paria. There are a number of deposits of asphalt scattered over the island, but the one of chief commercial importance is the so-called Pitch Lake in the county of St. Patrick on the western shore about 28 miles, airline, from Port of Spain, the seat of the colonial government and port of entrance of Trinidad.

Pieces of freshly dug crude Trinidad asphalt showing typical gas pockets

Digging crude asphalt from the Bermudez Lake deposit, Venezuela. At times asphalt is below water as shown in this picture

Typical quarry scene, Kentucky, U.S.A. rock asphalt. Notice depth of overburden and ledge of uncovered rock asphalt. *Courtesy of the Kentucky Rock Asphalt Company, Inc., Louisville, Kentucky, U.S.A.*



Gigantic primary crusher, 60 × 48 inches. *Courtesy of the Kentucky Rock Asphalt Company, Inc., Louisville, Kentucky, U.S.A.*

The pitch lake was discovered by Sir Walter Raleigh in 1595. It covers an area of about 100 acres, situated on the highest part of La Brea Point 115 ft. above sea-level, and lies in the crater of an extinct mud volcano. Borings made in 1925 at the centre of the lake disclosed a depth of 285 ft. of asphalt of uniform composition. The material forming this deposit is an emulsion of water and bitumen with a suspension of impalpably fine clay and a comparatively small quantity of silica.

The entire mass of asphalt is in slow but constant motion from the centre towards the edges accompanied by the evolution of gas: largely hydrogen sulphide and carbon dioxide. It is hard enough to be dug out with picks (mattocks) and to support the tracks of the industrial railroad laid upon its surface, used to transport the asphalt to a refinery situated on solid ground at the edge of the lake.

The occurrence of Trinidad Lake asphalt is thought to be due to the escape of hydrocarbons in past ages from underlying sands into the crater of a mud volcano or geyser where it mingled under gas pressure with a paste of impalpably fine clay and silica, and was churned into an emulsion. The originally soft material has been converted into hard asphalt probably by the catalytic action of the colloidal clay over a long period of time. The constant movement of the lake has resulted in the maintenance of an unusually uniform mass of asphalt throughout its entire depth.

Richardson [10, 1908] found that specimens collected at intervals of 100 ft. and a depth of 1 ft. at these intervals over the surface of the deposit and in addition at every foot to a depth of 135 ft. at the centre all had the same composition. The water present is as constant in amount as the other constituents.

The crude Trinidad Lake asphalt has the following average composition:

	%
Water and gas volatilized at 100° C.	29·00
Soluble in carbon disulphide	39·30
Mineral matter on ignition	27·20
Water of hydration and adsorbed bitumen	4·50
	100·00

Weight per cubic foot, average 75 lb.

Crude Trinidad Lake asphalt is transported in bulk in the holds of steamers which for this particular trade carry cargoes of from 5,000 to 6,000 tons. The asphalt flows together again in transit, and to unload the vessel it is dug out, as at the deposit.

The refined asphalt is prepared in a refinery by placing the crude asphalt in large, open kettles containing pipe coils and heating it with steam until the water is evaporated. These kettles hold about 75 tons each of asphalt, and heat is applied by means of steam at 150 lb. pressure circulated through the pipe coils and by live steam which is used for agitation after the temperature of the mass is above 200° F. The dried asphalt is then strained into barrels or other containers and is the steam-refined Trinidad Lake asphalt of commerce known as Trinidad Epuré or Trinidad Refined Asphalt. As put up in slack barrels, the average weight per package is 515 lb. gross and 490 lb. net.

The characteristics of steam-refined Trinidad Lake asphalt have not changed appreciably over the long period of years that this material has been produced. It has been examined and commented upon by many investigators, and its chemical and physical characteristics have been reported in considerable detail by Richardson and Abraham as follows:

TABLE V

Refined Trinidad Lake Asphalt [10]

Physical properties

Specific gravity 78° F./78° F., original substance, dry	1·40
Colour of powder	Blue-black
Lustre	Dull
Structure	Homogeneous
Fracture	Semi-conchoidal
Hardness, original substance	2
Odour	Asphaltic
Softens*	180° F.
Flows*	190° F.
Penetration at 78° F.	7

Chemical characteristics

Dry substance:	
Loss, 325° F., 7 hr.	1·1%
Character of residue	Smooth
Loss, 400° F., 7 hr. (fresh sample)	4·0%
Character of residue	Blistered
Bitumen soluble in CS_2, air temperature	56·53%
Inorganic or mineral matter	36·50%
Difference undetermined	6·97%
	100·00%
Malthenes:	
Bitumen soluble in 88° naphtha, air temperature	35·6%
This is per cent. of total bitumen	63·1
Per cent. of soluble bitumen removed by H_2SO_4	61·3
Per cent. of total bitumen as saturated hydrocarbons	24·4
Bitumen soluble in 62° naphtha	41·7%
This is per cent. of total bitumen	73·9
Carbenes:	
Bitumen more soluble in carbon tetrachloride, air temperature, than in CS_2	1·3
Bitumen yield on ignition:	
Fixed carbon	10·8%
Sulphur	6·2%
Ultimate composition:	
Carbon	82·33%
Hydrogen	10·69%
Sulphur	6·16%
Nitrogen	0·81%
	100·00%

* These values were obtained with the 'over mercury' method described on page 2723.

TABLE VI

Trinidad Lake Asphalt [1]

Colour in mass	Black
Fracture	Conchoidal
Lustre	Dull
Streak	Black
Specific gravity at 77° F.	1·40–1·42
Hardness, Moh's scale	1–2
Penetration at 115° F.	10–15
„ 77° F.	1·5–4·0
„ 32° F.	0·25–0·75
Consistency at 115° F.	32·7
„ 77° F.	74·9
„ 32° F.	Above 100
Susceptibility factor	Greater than 80
Ductility (Dow method):	
At 115° F.	8·0
At 77° F.	1·8
At 32° F.	0·1
Ductility (Miller method):	
At 115° F.	1·5
At 77° F.	1·0
At 32° F.	0·0

TABLE VI (*cont.*)

Tensile strength (Miller method):	
At 115° F.	4·15
At 77° F.	21·0
At 32° F.	27·0
Fusing-point (K. and S. method)	188° F.
„ (R. and B. method)	206° F.
„ , *pure* asphalt extracted from mineral matter (K. and S. method)	131·5° F.
Fusing-point, ditto (R. and B. method)	149° F.
Volatile at 325° F., in 5 hr.	1·1–1·7%
„ 409° F., in 5 hr.	4·0–5·25%
Fixed carbon	10·8 — 12·0%
Soluble in carbon disulphide	56–37%
Asphalt retained by mineral matter	0·3%
Mineral matter on ignition with tri-calcium phosphate	38·5%
Water of hydration (clay and silicates)	4·2%
Carbenes	0·0–1·3%
Soluble in 88° petroleum naphtha (pure asphalt)	62–64%
Carbon (ash-free)	80–82%
Hydrogen (ash-free basis)	10–11%
Sulphur (ash-free basis)	6–8%
Nitrogen (ash-free basis)	0·6–0·8%
Solid paraffins	0·0%
Saturated hydrocarbons	24·4%
Saponification value	40·0%
Free asphaltous acids	6·4%
Asphaltous acid anhydrides	3·9%
Asphaltenes	37·0%
Asphaltic resins	23·0%
Oily constituents	31·0%

Table VII also records a typical and recent (1930) analysis of Refined Trinidad Asphalt:

TABLE VII

Refined Trinidad Lake Asphalt

Specific gravity at 60° F.	1·407
Colour of powder or streak	Blue-black
Lustre	Dull
Structure	Uniform
Fracture	Semi-conchoidal
Hardness	2
Odour	Asphaltic
Softening point (R. and B. method)	210° F. (99° C.)
Consistency:	
Penetration at 32° F. (0° C.), 200 g., 60 sec.	0
„ 32° F. (0° C.), 100 g., 5 sec.	0
„ 77° F. (25° C.), 100 g., 5 sec.	2·0
„ 100° F. (38° C.), 100 g., 5 sec.	7·5
„ 115° F. (46° C.), 50 g., 5 sec.	10·0
Ductility at 77° F. (25° C.), 5 cm. per min.	too hard
Flash (Cleveland open cup)	490° F. (254·5° C.)
Bitumen (soluble in CS_2)	56·0%
Mineral matter	36·0%
Difference	8·0%
Per cent. of bitumen soluble in CCl_4	100·0
„ „ „ 86° naphtha	64·0
„ „ „ ethyl ether	80·0
Fixed carbon (ash-free)	11·0%
Paraffin scale (Holde method)	None
Sulphur	3·3%
„ (on bitumen)	5·89%
Loss 50 g., 5 hr., at 325° F. (163° C.)	0·5%
Residue: penetration at 77° F. (25° C.), 100 g., 5 sec.	0
Residue: ductility at 77° F. (25° C.)	Too hard

Fluxing of Trinidad Native Lake Asphalt.

The refined asphalt is too hard for many industrial applications. The most common type of softening medium is a liquid petroleum residuum of proper flash and fluidity, generally referred to as a flux. When the refined asphalt is softened by blending with such a flux the product is known as an asphalt cement, Trinidad Lake Asphalt Cement, or as a fluxed native asphalt. Typical analyses of several different consistency asphalt cements are given in Table VIII:

TABLE VIII

Trinidad Lake Asphalt Cements

(The liquid petroleum flux used was produced from an asphaltic base crude.)

	25 pen.	*50 pen.*	*80 pen.*
Specific gravity at 60° F. (15·5° C.)	1·274	1·232	1·198
Softening-point (Ring and Ball)	140° F. (60° C.)	129° F. (54° C.)	118° F. (48° C.)
Penetration at 32° F. (0° C.), 200 g., 60 sec.	8	13	19
Penetration at 32° F. (0° C.), 100 g., 5 sec.	3	4	6
Penetration at 77° F. (25° C.), 100 g., 5 sec.	25	50	80
Penetration at 100° F. (38° C.), 100 g., 5 sec.	88	170	Too soft
Penetration at 115° F. (46° C.), 50 g., 5 sec.	130	248	Too soft
Ductility at 77° F. (25° C.), 5 cm. per min. pull	32 cm.	68 cm.	97 + cm.
Flash-point (Cleveland open cup)	440° F. (226·5° C.)	410° F. (210° C.)	400° F. (204·5° C.)
Fire-point „ „	480° F. (219° C.)	460° F. (238° C.)	440° F. (226·5° C.)
Flash-point (Pensky Martin closed cup)	410° F. (210° C.)	390° F. (199° C.)	380° F. (193·5° C.)
Bitumen (soluble in CS_2)	67·3%	72·4%	75·8%
Mineral matter	27·1%	22·8%	19·9%
Difference	5·6%	4·8%	4·3%
Per cent. of bitumen soluble in CCl_4	99·8	99·9	99·9
Per cent. of bitumen soluble in 86° naphtha	71·0	73·9	74·6
Per cent. of bitumen soluble in ethyl ether	84·1	84·8	85·7
Fixed carbon (ash-free)	11·7%	11·0%	10·5%
Paraffin scale (Holde method)	0·2%	0·3%	0·35%
Sulphur	3·43%	3·35%	3·30%
Loss 50 g., 5 hr., 325° F. (163° C.)	0·34%	0·38%	0·43%
Residue: penetration at 77° F. (25° C.), 100 g., 5 sec.	21	42	67
Furol viscosity at 300° F. (149° C.)	..	240 sec.	..
„ „ 350° F. (176·5° C.)	..	87 sec.	..
„ „ 400° F. (204·5° C.)	..	42 sec.	..

Liquid petroleum fluxes derived from various kinds of crude petroleums and possessing different viscosities soften Trinidad Native Lake Asphalt to varying degrees. Figs. 1, 2, and 3 show the effect of three different petroleum fluxes on the consistency of Trinidad asphalt (as expressed by the penetration at 77° F. (25° C.) 100 g., 5 sec.). It will be noted that the most fluid flux gives the softest asphalt cement for any particular proportion of Trinidad and flux.

Mixtures of Trinidad Asphalt with Tar.

The hydrocarbons composing Trinidad Lake asphalt seem to be peculiarly adapted for blending with coal tar. Greater proportions of Trinidad than of other asphalts are miscible with tar, thereby providing greater stabilization of the tar, both from the standpoint of its susceptibility to temperature and its volatility. Further, by the addition of even small quantities of Trinidad Lake asphalt the consistency of a tar is markedly increased. Wichert [16, 1929] has published the results of an interesting investigation of the combination of various asphalts and tars. He found that, as is generally known, asphalts and tars are limited

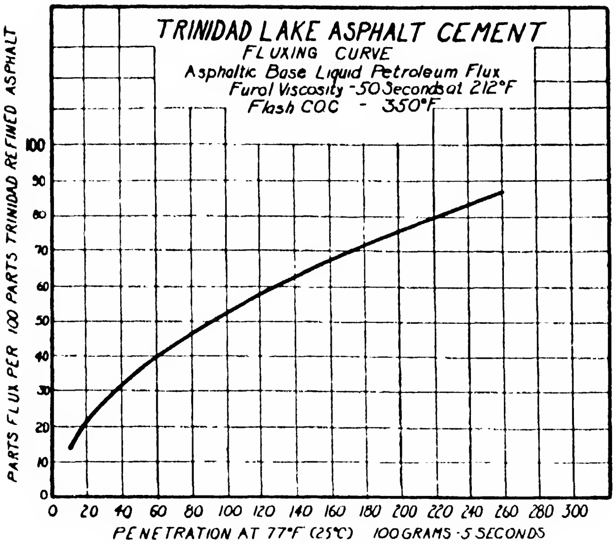


FIG. 1.

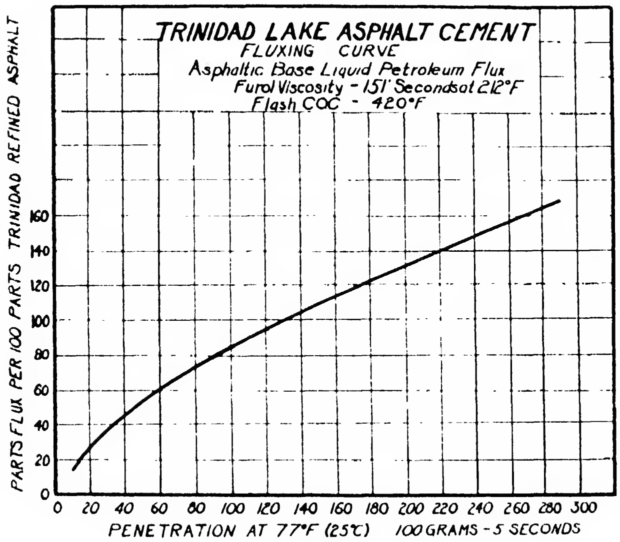


FIG. 2.

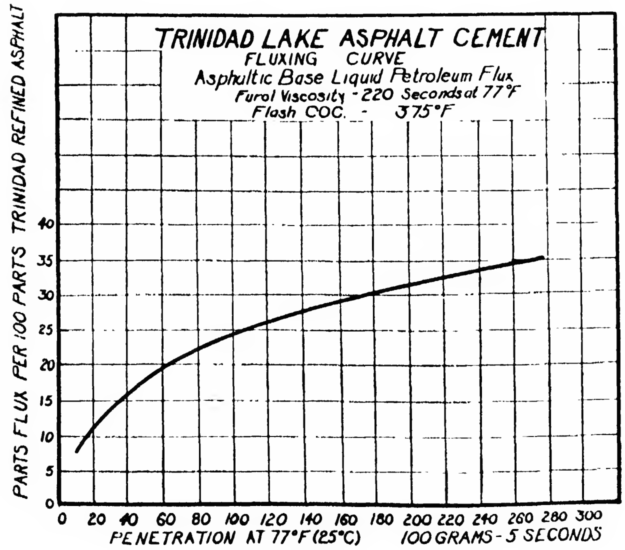


FIG. 3.

with respect to miscibility but that Trinidad asphalt can be used in greater proportions, thus providing greater flexibility in this very important field. The viscosity of a particular tar was increased 4½-fold by the addition of 15% of Trinidad asphalt. Wichert gives several photomicrographs of mixtures of Trinidad asphalt-tar and oil asphalt-tar which indicate that the former are more homogeneous than the latter.

The Mineral Matter in Trinidad Native Lake Asphalt.

The mineral matter in Trinidad Native Lake asphalt is chiefly clay and fine silica sand, but many rather rare minerals are also present, and the presence of these has been used by Wilson [17, 1934] to identify the presence of Trinidad Epuré. The heavy minerals which he separates from the mineral aggregate by means of bromoform are titanite, zircon, rutile, and glaucophane. The latter is a rather rare mineral.

Years ago (1908) Clifford Richardson [10] reported the particle-size distribution of the mineral matter extracted from Trinidad Native Lake asphalt. He used screens for the coarser material and water elutriation for the finer. The Limmer and Trinidad Lake Asphalt Company Ltd. in their annual report for 1934 give results on particle-size distribution obtained by means of a photo-electric turbidimeter. Careful measurements have also been made in the research laboratory of the Barber Asphalt Company. Separation of the unignited mineral matter into several size fractions followed by microscopic count and measurement of the thoroughly dispersed powder gave the data listed in Table IX. Richardson's and the Limmer and Trinidad's data are given for comparison. The results of Limmer and Trinidad and of the Barber Asphalt Company are in excellent accord. The fact that Richardson used the elutriation-in-water method no doubt accounts for his results being so divergent, especially for the smaller sizes.

TABLE IX

Particle-size Distribution in Mineral Matter from Trinidad Native Lake Asphalt

Particle size (microns)	*Weight, %*		
	Richardson	*Limmer and Trinidad*	*Barber asphalt*
-1	14·28	44·1	5·3
1–2			6·4
2–4			6·6
4–6			6·7
6–8			5·9
8–10			9·2
10–15	41·94	6·2	20·9
15–20		5·3	
20–5		5·6	18·6
25–30	11·76	4·7	
30–5		4·3	
35–40		1·8	
40–5		1·9	9·2
45–50		4·2	
50–5	21·82	2·4	
55–60		2·7	
60–75		8·0	
+75	10·20	8·8	11·2
Total	100·00	100·0	100·0

Colloidal Properties.

Asphalt is usually considered to be a colloidal system composed of high-carbon-content hydrocarbons, known as asphaltenes, dispersed in more fluid petrolenes which are made up of compounds having a higher hydrogen to carbon ratio. The asphaltic resins which are also present probably stabilize the system by helping to keep the asphaltenes in a dispersed condition. Certain solvents possess the ability of flocculating and precipitating the asphaltenes, and because of this property are of value in the identification of certain types of bitumen.

In Trinidad Native Lake asphalt there is present considerable mineral matter which may be classed as colloidal. Millions of the mineral particles in a pound of this asphalt are so small that they are invisible under the most powerful microscope. However, they can be detected in a dilute benzole or other solution of the asphalt by means of the ultra-microscope. These fine particles, which exhibit Brownian movement, are not deposited from the dilute benzole solution even after many years.

When no solvent is present mineral particles so large as to be readily visible by means of the microscope remain suspended indefinitely in the bitumen. Changes in the viscosity of the continuous phase (the bitumen), whether due to solution or heat, cause disturbances in the system, and consequently more or less of the larger particles will settle out. It has not, so far, been determined whether changes in the rate of settling, due to alteration of viscosity by heat, will follow Stokes's law, but in dilute solutions the rate of settling does follow that law very closely.

Clifford Richardson's work with this asphalt and his study of the colloidal phenomena of its mineral matter needs no review here. No means have yet been found to economically obtain in a bitumen such a high percentage of colloidally dispersed mineral particles as may be seen in dilute solutions of this lake asphalt. It has been practically impossible to obtain the consistency characteristics (penetration and softening-point) of Trinidad Lake asphalt by compounding the same percentage composition by weight of bitumen and mineral filler. Apparently the degree of subdivision of the mineral matter, amount of adsorption of the hydrocarbons to the surface of the solid particles, and the character of the hydrocarbons present constitute a system difficult to reproduce.

Flow Properties of Asphalt at Temperatures of Use.

The tests, such as penetration and softening-point, commonly used for measuring the consistency of fairly hard asphalts give rather indefinite measurements of their rheological properties. Although viscosities at high temperatures, corresponding roughly to the temperatures of application or compounding, have been measured for a long time, only recently have methods been developed for determining the rheological characteristics of materials as hard as paving asphalt at atmospheric temperatures.

In respect to their flow characteristics, liquids may be classified as:

(1) **Viscous.** If a viscous liquid is subjected to shear in a viscometer and the volume of flow is plotted against the shearing stress, a straight line passing through the origin will be obtained. In other words, these materials flow under the application of any shearing stress no matter how small. The viscosity or resistance to internal flow in the fluid is expressed in poises (dyne-seconds per sq. cm.). Some asphalts are found to be viscous liquids.

(2) **Quasi-viscous.** Liquids placed under this classification possess what is sometimes called structural viscosity. Although they will move under the application of the smallest measurable force, nevertheless a plot of the volume of flow against the shearing stress gives a curve passing through the origin but convex towards the shearing-stress axis. This means that as greater force is applied the apparent viscosity of the fluid becomes less. Air-blown asphalts and some hard steam-refined bitumens have been found to possess structural viscosity or to be quasi-viscous.

(3) **Plastics.** These substances require the application of a definite shearing stress before flow occurs. The point at which the linear portion of the flow-shear curve intersects the shearing-stress axis is called the yield value. Some investigators believe that many substances considered as plastics really come under classification (2) above.

The rheological properties of various asphalts and bitumens have been investigated recently by Broome and Thomas [4, 1931], Saal [11, 1933], Saal and Koens [12, 1933], Pittman and Traxler [8, 1934], and Traxler, Pittman, and Burns [15, 1935]. In general, the conclusion has been drawn that some bitumens are viscous while others are either quasi-viscous liquids or plastic solids. Asphalts from the same source and processed in the same manner may exhibit different flow properties; a soft asphalt may be viscous, whereas a hard one of the same type may show structural viscosity. Almost all bitumens possess elastic properties, and in most viscometers this property is a source of annoyance in measuring the permanent (viscous) deformation of the liquid. Thixotropy is another property encountered in certain asphalts.

In Table X the viscosities of five different kinds of asphalt [8, 1934] are given in poises at temperatures ranging from 15° C. (59° F.) to 130° C. (266° F.). The asphalts were all of approximately 60 penetration at 25° C. (77° F.), 100 g., 5 sec. Asphalt *A* was produced from Mexican petroleum, Asphalt *B* from Venezuelan, and Asphalt *C* from Trinidad petroleum by steam distillation. Asphalt *D* is Bermudez Native Lake asphalt cement, and Asphalt *E* is Trinidad Native Lake asphalt cement, each softened with a liquid petroleum flux produced from the same petroleum used to prepare Asphalt *B*.

TABLE X

Viscosity-Temperature Data

Temp. ° C.	*Viscosity in poises*				
	A	*B*	*C*	*D*	*E*
15	$9{\cdot}20\times10^7$	$6{\cdot}33\times10^7$	$6{\cdot}49\times10^7$	$3{\cdot}69\times10^7$	$4{\cdot}32\times10^7$
20	$2{\cdot}26\times10^7$	$1{\cdot}76\times10^7$	$1{\cdot}47\times10^7$	..	$1{\cdot}25\times10^7$
21	..	..	..	$9{\cdot}56\times10^6$	$9{\cdot}49\times10^6$
25	$6{\cdot}98\times10^6$	$6{\cdot}24\times10^6$	$3{\cdot}35\times10^6$	$3{\cdot}66\times10^6$	$4{\cdot}06\times10^6$
30	$2{\cdot}75\times10^6$	$1{\cdot}81\times10^6$	$9{\cdot}02\times10^5$	$1{\cdot}28\times10^6$	$1{\cdot}32\times10^6$
35	$8{\cdot}45\times10^5$	$4{\cdot}97\times10^5$	$2{\cdot}50\times10^5$	$4{\cdot}91\times10^5$	$4{\cdot}84\times10^5$
40	$2{\cdot}33\times10^5$	$1{\cdot}71\times10^5$	$8{\cdot}06\times10^4$	$1{\cdot}28\times10^5$	$1{\cdot}38\times10^5$
50	$4{\cdot}23\times10^4$	$2{\cdot}41\times10^4$	$1{\cdot}40\times10^4$	$2{\cdot}10\times10^4$	$2{\cdot}26\times10^4$
60	$8{\cdot}67\times10^3$	$4{\cdot}72\times10^3$	$2{\cdot}73\times10^3$	$4{\cdot}28\times10^3$	$4{\cdot}82\times10^3$
70	$2{\cdot}27\times10^3$	$1{\cdot}20\times10^3$	$7{\cdot}68\times10^2$	$1{\cdot}19\times10^3$	$1{\cdot}45\times10^3$
80	$7{\cdot}01\times10^2$	$3{\cdot}59\times10^3$	$2{\cdot}52\times10^2$	$3{\cdot}71\times10^2$	$4{\cdot}75\times10^2$
90	$2{\cdot}41\times10^2$	$1{\cdot}32\times10^2$	$7{\cdot}91\times10$	$1{\cdot}50\times10^2$	$2{\cdot}07\times10^2$
100	$1{\cdot}03\times10^2$	$6{\cdot}00\times10$	$3{\cdot}35\times10$	$6{\cdot}27\times10$	$9{\cdot}10\times10$
110	$4{\cdot}32\times10$	$2{\cdot}59\times10$	$1{\cdot}61\times10$	$2{\cdot}93\times10$	*
120	$2{\cdot}27\times10$	$1{\cdot}43\times10$	8·47	$1{\cdot}46\times10$	*
130	$1{\cdot}13\times10$	6·77	4·84	8·74	*

* Not obtained due to the too rapid settling of a portion of the mineral matter which is naturally present in this asphalt.

Numerous empirical formulae have been applied to these data, but none was found to be of practical value due to the number of constants necessary to give deviations within the limits of experimental error. Thus it is concluded that the viscosity-temperature relationship for most known bitumens is very complex if the measurements are extended over a wide enough range.

Fig. 4, which is reproduced from a paper by Traxler, Pittman, and Burns, shows the relationship between penetration, 100 g., 5 sec., and viscosity in poises for Trinidad Lake asphalt cements. Curve *A* represented by a solid line shows the relationship between penetration and viscosity when the consistency is changed by varying the temperature of test. The broken line (curve *B*) shows the same relationship when the consistency is altered by using different amounts of flux on the Trinidad Refined Asphalt. Curves of the same general shape have been obtained for other asphalts.

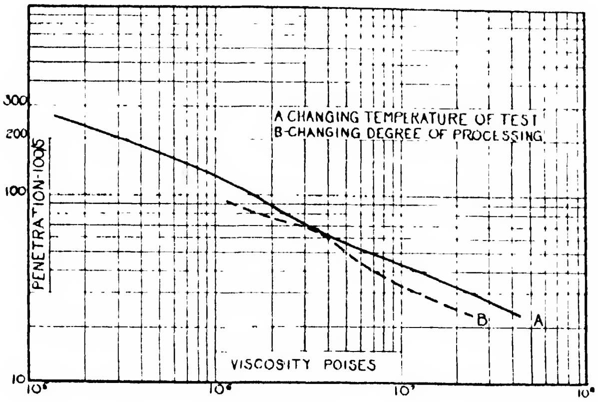


FIG. 4.

From these data it is evident that altering consistency either by temperature changes or by processing results in decidedly different penetration-viscosity relationships.

Increase in Viscosity of Asphalts with Time.

Unpublished results obtained in the research laboratory of the Barber Asphalt Company indicate that all asphalts tend to become harder on standing at 25° C. (77° F.). This effect is not due to evaporation of volatile constituents because, on remelting and cooling to 25° C. (77° F.), the materials return to their original and more fluid condition.

In order to obtain quantitative measurements of this hardening effect a number of co-axial cylinder viscometers of the type proposed by Pochettino [9, 1914] were filled with bitumen, allowed to cool, and then placed in a cabinet maintained constantly at the desired temperature. Instruments were removed from time to time and the viscosity of the asphalt determined by measuring the rate of fall of the inner cylinder by means of a cathetometer. The viscometer and contents were suspended in a constant temperature bath during the measurement of viscosity. Fig. 5 shows the common logarithm of the viscosities in poises plotted on an arithmetic scale versus hours of ageing on a logarithmic scale. A log-log plot of these data was chosen because the slopes of the resulting lines are direct measures of the percentage increase in viscosity of the asphalts for given percentage increases in time.

Thus, Trinidad Native Lake asphalt cements and steam-refined Trinidad and Californian asphalts show relatively little hardening with time, whereas asphalts produced by steam distillation of Venezuelan, Arkansas, and Mexican petroleum show comparatively rapid and extensive hardening. This phenomenon probably has its origin in the development of a structure within the asphalt which, as pointed out above, is unstable to heat and possibly to vigorous mechanical working. The latter point has not as yet been experimentally proven. Where the asphalt in use is not subjected to sufficient thermal changes or mechanical working, this time-hardening effect may be a very serious factor in making the pavements or other structures too hard so that they are liable to crack or disintegrate.

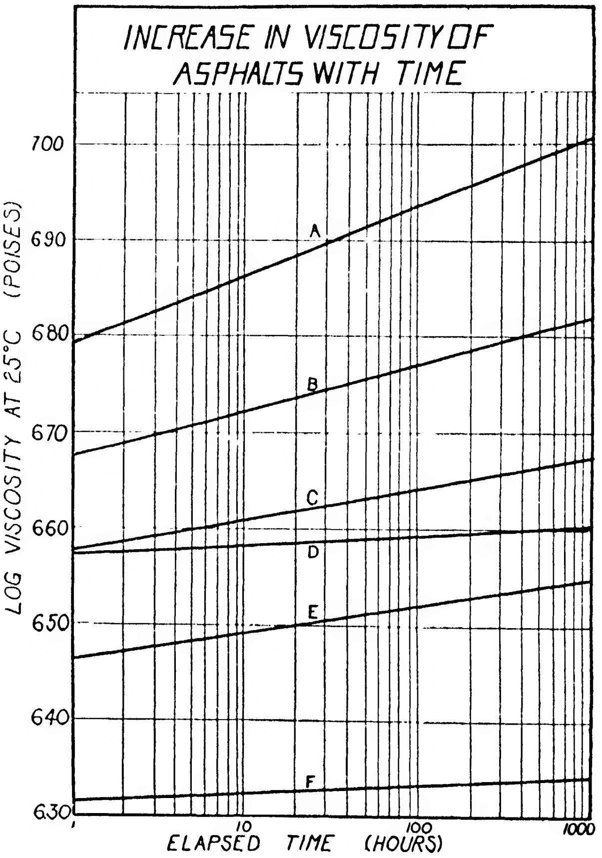


FIG. 5.

Permanent Hardening of Paving Asphalts during preparation of the Paving Mixture.

Since Abson [2, 1933] has devised a method to recover an asphalt from solution without materially affecting its properties, it has been found that some paving asphalts are greatly altered during the process of hot mixing with mineral aggregate preparatory to laying the pavement. If samples of paving mixture are taken as they leave the mixer, or if samples are removed from the freshly laid pavement, or from an old one, and the bitumen is extracted by means of benzole and recovered immediately, using Abson's distillation with CO_2, it will be found that most asphalts have hardened and lost ductility. At the present time little is known as to the causes of these changes in properties; they may be due to evaporation, oxidation, polymerization, or sulphur reactions with the hydrocarbons of the asphalt. However, a superior asphalt for paving purposes certainly should not show any serious loss of its valuable properties, such as ductility, adhesiveness, &c., during the process of mixing with the mineral aggregate or during the laying of the pavement. Such considerations serve to emphasize the necessity for recognizing different asphalts as distinctly different materials in their behaviour both in the paving plant and in the pavement itself. Quite obviously, then, it is erroneous to assume that a number of different asphalts of the same penetration will behave in the same way in actual commercial operations.

Combination of Two Asphalts of High Softening-point to give a Mixture of Low Softening-point.

Frequently it is desirable to blend high softening-point asphalts with Trinidad Native Lake asphalt. With certain types of bitumen, such combinations will yield compounds possessing lower softening-points than either of the components.

An air-blown asphalt of 140 penetration at 25° C. (77° F.), 100 g., 5 sec., and 143° C. (290° F.) Ring and Ball softening-point was compounded in various proportions with Refined Trinidad Lake Asphalt of 4 penetration and 97° C. (207° F.) Ring and Ball softening-point.

A steam-refined oil asphalt of 1 penetration at 25° C. (77° F.), 100 g., 5 sec., and 114·5° C. (238° F.) Ring and Ball softening-point was also mixed in the same proportions with Refined Trinidad Lake Asphalt. The Ring and Ball softening-points for each compound of both series are recorded in Table XI. The data are shown graphically in Fig. 6.

TABLE XI

Refined Trinidad asphalt %	Blown asphalt %	Blown asphalt R. and B. softening-point, ° F.	Steam-refined asphalt %	Steam-refined asphalt R. and B. softening-point, ° F.
100	0	207	0	207
85	15	168	15	201
70	30	153	30	204
50	50	162	50	210
30	70	205	70	217
15	85	245	85	226
0	100	290	100	238

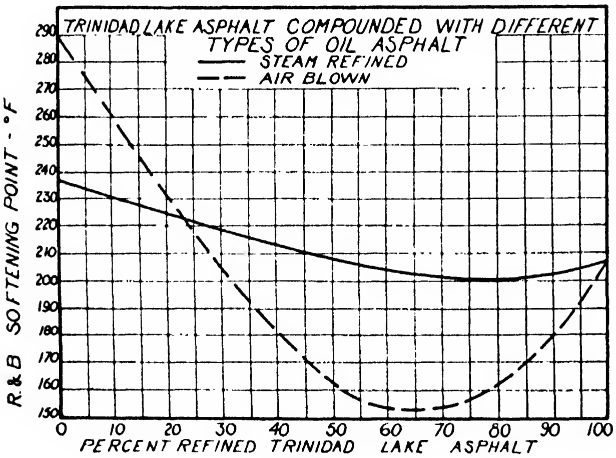


FIG. 6.

The compounds containing less than about 50% Refined Trinidad asphalt mixed with steam-refined oil asphalt combine as if the Trinidad asphalt possessed a softening-point of about 175° F. (the softening-point of the mineral-free bitumen) instead of 207° F. This behaviour is probably due to the fact that in these blends containing smaller amounts of Trinidad Native Lake the mineral matter content originally present is greatly diluted and thus does not exert any appreciable stabilizing effect on the compounded material.

From the work which has been done with finely divided mineral fillers it has been found that their stabilizing effect is not evident until they are present to the extent of about 20%. Of course there are exceptions when the mineral filler possesses peculiar structural characteristics (e.g. as in kieselguhr, asbestos, &c.).

The remarkable depression of the softening-point obtained with certain blends of Trinidad-blown asphalt cannot be explained entirely on the basis of dilution of mineral content. This phenomenon is probably to be explained by physico-chemical considerations of the structure of asphalt.

Acid and Saponification Values of Natural Asphalts.

Paillar [7, 1914] has developed a method for determining the acid number of asphalts. He places 30 g. of bitumen or enough asphalt to yield that much bitumen in a retort and heats until the material is melted. The flame is adjusted so that about one drop of distillate is collected every 2 seconds. The distillate is collected in 5 c.c. portions and each portion weighed and then dissolved in 10 c.c. portions of ether. After washing the etheral solution with water in a separatory funnel until free of any mineral acid present, the etheral solution is transferred to an Erlenmeyer flask, diluted with 75 c.c. of neutral alcohol, 5 c.c. of 1% alcoholic solution of alkaline blue is added, and the mixture titrated until the red colour changes to blue. The acid number is expressed in milligrams of KOH used to neutralize the acid in 1 g. of oil distillate. Table XII gives a portion of Paillar's data:

TABLE XII

Acid Value of Various Asphalts

Kind of asphalt	Acid value 1st distillate	Acid value 2nd distillate
Trinidad	16·20	8·40
Bermudez	9·80	3·20
California	0·11	0·07
Mexican	0·24	0·05
Bermudez + California	4·90	1·20
Bermudez + Mexican	5·40	2·00

These data show that the acid values of native asphalts are considerably higher than those prepared by the distillation of petroleum.

The saponification value of the various asphalts may be determined by dissolving 5 g. of ash-free bitumen in 30 c.c. of benzole and then boiling with 50 c.c. of normal alcoholic KOH under a reflux condenser. The mixture is cooled to room temperature, 250 c.c. of 95% alcohol are added, and the excess KOH titrated with normal H_2SO_4, using alkaline blue as an indicator. Paillar obtained the results given in Table XIII:

TABLE XIII

Saponification Value of Various Asphalts

Asphalt	Saponification No.
Trinidad	40·0
Bermudez	28·0
California	12·0
Mexican	10·5
Bermudez + California	20·5
Bermudez + Mexican	19·7
Trinidad + California	26·0
Trinidad + Mexican	24·9

Molecular Weights of Asphaltic Bitumen.

Strieter [13, 1925] obtained values for the average molecular weight of the bitumen in several asphalts. The bitumen was dissolved in benzole and the molecular weight determined by the lowering of the freezing-point. Apparently little trouble was encountered in obtaining sharp temperature readings. Table XIV gives values for three bitumens, each value representing the average of two closely checking duplicate determinations:

TABLE XIV

Molecular Weights of Asphalts

Asphalt	*Molecular weight*
Trinidad bitumen	1131·8
Bermudez „	620·4
Gilsonite „	4251·5

The oils obtained from these asphalts by distillation have molecular weights of about 230, and it is suggested by Strieter that the hydrocarbons present are polycyclic compounds with about four rings. Thus the hydrocarbons in Trinidad asphalt with a molecular weight of 1131·8 would contain 12 to 16 rings.

Specific Heats.

The specific heats of various asphalts are listed in Table XV. Because of its mineral content Trinidad Native Lake asphalt has the lowest specific heat of any asphalt.

TABLE XV

Specific Heats of Asphalts

Refined Trinidad Lake asphalt	0·350
Trinidad asphalt cement	0·381
Bermudez asphalt cement	0·413
Typical oil asphalt	0·450

Coefficient of Expansion.

The coefficients of expansion of Trinidad, Bermudez, and a typical steam-refined oil asphalt for temperatures from 35° to 160° F. are given in Table XVI. These data were calculated using the equation

$$A = \frac{D_T - D_t}{D_t(t-T)},$$

where A = the volume coefficient of expansion,
D_t = density at the higher temperature,
D_T = density at the lower temperature,
t and T = temperature in ° F.

TABLE XVI

Volume Coefficients of Expansion

Asphalt	*Temp. ° F.*	*Density*	*Temp. range ° F.*	*Coefficient of expansion*
Trinidad	35	1·254	(35–60)	0·000289
„	60	1·245	(60–100)	0·000305
„	100	1·230	(100–60)	0·000304
„	160	1·208	(35–160)	0·000305
Bermudez	35	1·069	(35–60)	0·000301
„	60	1·061	(60–100)	0·000359
„	100	1·046	(100–60)	0·000342
„	160	1·025	(35–160)	0·000343
Typical steam-refined oil asphalt	35	1·064	(35–60)	0·000341
	60	1·055	(60–100)	0·000360
„ „	100	1·040	(100–60)	0·000344
„ „	160	1·019	(35–160)	0·000353

It should be noted that densities and not specific gravities are used in these calculations. The reader interested in expansion coefficients for bituminous products should refer to the Report of Sub-committee X of the American Society for Testing Materials [14, 1934] for data and a discussion of the accuracy of the measurements.

Cementitiousness of Asphalt.

A most important property of asphalt is its ability to bind together particles of solid material, usually composed of mineral aggregate. L. Kirschbraun [5, 1914] developed a method for measuring this property which he called the cementitiousness or cementing value of the asphalt. His method will not be described here, but the student of asphalt is urged to read the original article which gives a complete description and discussion of the method with considerable data concerning the cementing values of various asphalts.

Fig. 7 shows the cementing values obtained for Trinidad Lake asphalt cements of 30, 50, 70, and 140 penetration at 25° C. (77° F.), 100 g., 5 sec., in which the Trinidad asphalt is softened (1) with a flux derived from paraffin-base crude, and (2) with a flux from asphaltic-base crude. Also, the cementitiousness of a typical steam-refined oil asphalt (3) is given for 30, 50, 70, and 140 penetration.

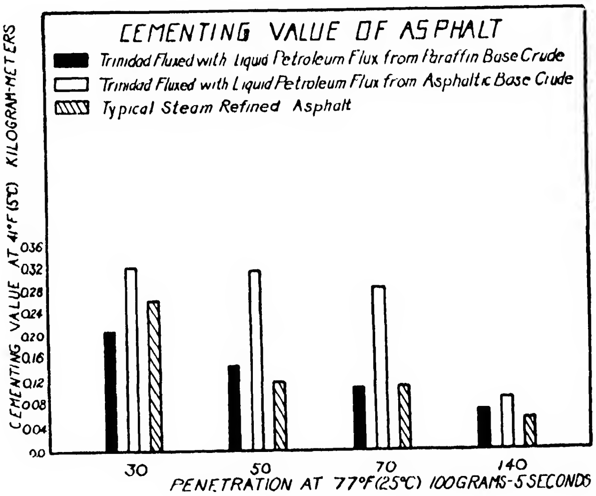


FIG. 7.

Trinidad Lake Asphalt—Uses.

Trinidad asphalt was originally exploited for street paving in 1870, when it was so used for the first time in Newark, N.J. In subsequent years similar pavements were laid in New York City, while in 1876 an extensive yardage was constructed in Washington, D.C. Since that time it has been used throughout the world as a standard paving material.

Other extensive uses for this asphalt are in the manufacture of asphalt roofings and shingles, waterproofing materials, asphalt mastic, and coatings for pipes and conduits, while the more highly specialized uses to which it has been put are too varied to enumerate. Being miscible in all proportions with practically all other asphalts and native bitumens, as well as with vegetable and mineral oils, waxes, and pitches, and in relatively large proportions with coal tar, Trinidad asphalt becomes applicable to many diversified uses. Nearly all of the industrial uses require manipulation at an elevated temperature, and blends of Trinidad asphalt with softer or harder bituminous materials are usually made at temperatures from 225° to 400° F.

This asphalt is, also, capable of being pulverized in a hammer-type disintegrator or mill and has had extensive use in that form, especially in the manufacture of the so-called cold paving compositions which can be laid either cold or hot.

Asphalt from Mesopotamia (Iraq)

Deposits of asphalt are found along the Euphrates River in old Mesopotamia, now known as Iraq. A typical analysis is given in Table XVII:

TABLE XVII

Asphalt from Iraq

Odour on heating	Asphaltic
Softening-point (R. and B.)	305° F.
Penetration at 77° F. 100/5	..
Bitumen (soluble in CS_2)	67·0%
Mineral matter (ash)	22·6%
Difference (organic insoluble)	10·4%
Bitumen soluble in CCl_4	93·7%
,, ,, ethyl ether	56·1%
,, ,, 86° naphtha	36·6%
Fixed carbon (ash-free)	14·8%
,, ,, (bitumen basis)	17·5%

Boeton Asphalt from Dutch East Indies

On the Island of Boeton in the Dutch East Indies there occurs an extensive deposit of bitumen mixed with microscopic shells. It is an interesting fact that on this island there occurs bitumen-filled coral despite the fact that coral cells are closed. No explanation has been offered as to how the asphalt found its way into the interior of the coral cells.

An analysis of Boeton asphalt is given in Table XVIII:

TABLE XVIII

Boeton Asphalt

Bitumen (soluble in CS_2)	37·1%
Mineral matter	49·0%
Difference	13·9%
Character of extracted bitumen:	
Softening-point (R. and B.)	152° F.
Penetration at 77° F. 100/5	18
Fixed carbon (ash-free)	10·74%
Character of mineral matter [3]:	
Silica (SiO_2)	5·32%
Alumina (Al_2O_3) and ferric oxide (Fe_2O_3)	2·62%
Lime (CaO)	49·22%
Magnesia (MgO)	1·43%
Sulphuric anhydride (SO_3)	0·51%
Carbonic anhydride (CO_2), alkalies, &c.	40·90%

Selenitza Asphalt from Albania

Commercial use, although on a somewhat limited scale, is made of a hard asphalt mined in Albania and marketed under the name Selenitza. Asphalt in Albania, on the shore of the Adriatic Sea, was referred to by Aristotle of Greece about 350 B.C., but the Selenitza material which occurs at Valona can scarcely be traced back directly to such early times.

The present Selenitza is a hard native asphalt containing from 10 to 25% mineral matter, and has been used locally after blending it with softer bitumen for street and road paving, mastic and liquid bituminous coatings or paints. Three typical analyses are given in Table XIX:

TABLE XIX

Albanian Asphalt—Selenitza

	151507	*153758*	*155315*
Water (by distillation)	4·6%	6·4%	7·1%
Dried material:			
Penetration at 77° F. 100/5	4	2	2
Softening-point (R. and B.)	250° F.	233° F.	222° F.
Bitumen (soluble in CS_2)	86·8%	82·1%	80·7%
Mineral matter (ash)	12·4%	14·4%	16·2%
Difference	0·8%	3·5%	3·1%
Bitumen soluble in CCl_4	97·1%	99·7%	..
,, ,, ethyl ether	43·3%	57·0%	55·1%
,, ,, 86° naphtha	42·6%	44·3%	42·4%
Fixed carbon	20·5%	20·2%	20·4%
Sulphur (calculated on pure bitumen)	6·9%	7·2%	6·7%
Paraffin scale	..	..	0·2%
Fluxing:			
Parts of asphalt	100	..	..
Parts of liquid petroleum flux	45	..	..
Resultant fluxed selenitza:			
Penetration at 77° F. 100/5	51	..	..
Ductility at 77° F. in cm.	18	..	..

Rock Asphalt

There are numerous deposits of native rock asphalt throughout the world, but those of chief commercial importance are situated in the Continents of Europe and North America.

Although several of the European deposits (e.g. at Ragusa) have been known for a long time, it was not until after 1800 that these deposits were exploited commercially. The first pavements using rock asphalt were laid about 1835.

In the past some differences of opinion have existed concerning the definition of a rock asphalt, but the following definition quoted from British Standard Specification No. 596—1935 represents the present opinion at least of the technologists of Great Britain:

> 'The aggregate shall consist of natural asphalt rock, this term being interpreted in a strictly geological sense and denoting a naturally occurring, consolidated, calcareous rock impregnated with bitumen exclusively by a natural process; the term shall exclude all other types of rock such as result from sporadic bitumen in any mode of occurrence in non-bituminous limestone or in a limestone of low grade impregnation, non-bituminous limestones and artificial mixtures thereof with bitumen of any source and description.'

The chief sources of rock asphalt coming under this definition and available in Europe to-day in commercial quantities are as follows:

1. The Cretaceous deposits of Pyrimont-Volant (Seyssel) region of the departments of Ain and Haute Savoie, France.
2. The Tertiary deposits of St. Jean de Marvejols, the department of Gard, France.
3. The Tertiary deposits of the Ragusa region, Province of Syracuse, Sicily.
4. The Cretaceous deposits of the Neuchâtel–Val de Travers region, Switzerland.
5. The Jurassic deposits of Vorwohle and Eschershausen in Brunswick, Germany.

Table XX gives typical physical and chemical characteristics of the bitumen and aggregate from types of European natural rock asphalt. The data were made available by the Building Research Station (Great Britain) through the Limmer and Trinidad Lake Asphalt Company, Ltd., who also supplied much of the subject-matter concerning European rock asphalts.

TABLE XX

Physical and Chemical Characteristics of the Bitumen and the Aggregate from Typical Specimens of Natural Rock Asphalt

Physical and chemical characteristics	*Sicilian*	*Seyssel (Pyrimont)*	*Val-de-Travers*	*St. Jean*	*Vorwohle*
Extracted bitumen:					
Soluble bitumen .	8–9%	4–8%	8–9%	8–11%	4–7%
Softening-point (R. and B.) . .	38° C.	46° C.	32° C.	48·5° C.	45·5° C.
Penetration at 0° C.	18	6	17	5	6
„ 25° C.	Too soft	118	Too soft	111	146
Viscosity by float test	125	163	76	262	171
Acid value . .	2·75	6·1	6·68	0·93	6·8
Saponification value	19·72	29·6	21·71	28·03	29·43
Asphaltenes . .	4·16	10·47	0·68	14·11	4·92
Oily constituents .	35·29	39·54	50·90	14·21	35·92
Aggregate:					
Silica (SiO_2) . .	Trace	Trace	0·78	Trace	4·3
Iron (Fe_2O_3) . .	Trace	Trace	0·5	Trace	Trace
Alumina (Al_2O_3) .	3·37	1·17	Trace	2·37	2·60
Lime (CaO) . .	61·1	66·4	64·6	60·7	69·4
Magnesia (MgO) .	Trace	Trace	0·32	Trace	Trace
Carbon dioxide .	35·5	32·4	33·8	36·9	29·4

The rock asphalts of North America occur chiefly in the States of Alabama, Arkansas, California, Kentucky, Louisiana, Oklahoma, Texas, and Utah in the U.S.A., while large deposits of asphaltic sands are found in Canada. These are all quite unlike the European rock asphalts in that they are generally composed of sand or sandstone, or limestone, or a mixture impregnated with bitumen, but if limestone they differ essentially in physical structure.

A few, but by no means all, of the commercially operated deposits are briefly mentioned below.

Texas. A deposit in Uvalde County is exploited as 'Uvalde Rock Asphalt'. This material is a conglomerate from 10 to 20% of hard bitumen and a limestone containing numerous fossil remains of molluscs. Uvalde Rock Asphalt is mixed with softer bitumens and crushed non-bituminous rock to produce a material for road-paving purposes.

Rock asphalts are found in other counties in the State, a few of which are enumerated below.

County	*Soluble in* CS_2	*Nature of* CS_2 *insoluble*
Montague . .	5–11	Sand and limestone
Burnet . .	10	Limestone

Oklahoma. The deposits in this State consist of asphaltic sands, asphaltic limestone, mixtures of the two, and occasionally of asphalt impregnated shale. A number of the deposits are listed below:

Deposit	*Soluble in* CS_2	*Nature of* CS_2 *insoluble*
Ralston . .	5·0	Sandstone
Buckhorn . .	11–12	„
Buckhorn . .	4–13	Limestone
Brunswick . .	1–3	„
Brunswick . .	2–11	Sandstone
Sneider . .	11	„
Emet . . .	10·4	„
Ravina . .	2·3–13·2	Limestone
Ardmore . .	9–12	Sandstone

Kentucky. Large deposits of asphaltic sandstone ledges 20 to 60 ft. in depth occur in Edmonson, Grayson, and Hart Counties not far from the famous Mammoth Cave, and on a peninsula which is situated between the Nolin and Green Rivers about 35 miles from Bowling Green. The trade name of 'Kyrock' is given to the rock asphalt mined in this region. The output per year is in excess of 250,000 tons.

Explorations are maintained on the deposits 6–10 years in advance of production. Core drillings together with laboratory analyses of the cores definitely define the extent and character of those portions of the veins under exploration.

In production the overburden of sandstone and earth are blasted loose and hauled away, making it possible to blast out the rock asphalt without contamination. Field-laboratory tests on the quarry face are further checks on the bitumen content. The blasted rock asphalt is hand selected by men experienced in judging bitumen content. The large pieces broken loose in the blasting operation are reduced in a succession of large crushers and then pulverized in roller mills to the size of the original sand grains. Continuous mixing during these operations, together with technical control, ensures suitability and uniformity of finished product. Only material containing 6·5–7·75% bitumen is sold as 'Natural' Kyrock.

Nothing needs to be added to 'Natural' Kyrock before it is laid as a pavement. The pulverized material is placed on the prepared base, cold, raked to the proper grade and then rolled. As soon as the rolling is completed the road or street may be opened to traffic. However, rock asphalt containing 3–6% bitumen must be processed with sufficient other asphalt to give a durable bond to the product. Both native and oil asphalts of proper quality and consistency may be used for this enrichment.

Deposits of rock asphalt also occur in Breckinridge, Carter, Hardin, Logan, and Warren Counties.

The description of the Kentucky operations is more or less typical of the methods generally used in the U.S.A., and for this reason have been described in considerable detail. The author is indebted to the Kentucky Rock Asphalt Company for most of the information given.

Rock Asphalt—Uses.

The commercial uses of rock asphalt are almost exclusively for the paving of footpaths and city streets; as a roofing material for buildings; for floors and for lining water tanks and reservoirs. The European rocks have been widely used for these purposes in the several countries in which they occur and also to a considerable extent abroad.

For roofing, flooring, and waterproofing purposes, the pulverized rock is blended with Trinidad Lake or other asphalts, thus producing 'mastic'. Such mastic is applied to a concrete or wood base, at a temperature of from 350° to 450° F., with hand tools such as 'floats' and 'spatulas' made of wood. It is much richer in bitumen than the rock mixtures that are applied by tamping, as a pavement for streets, and it is, therefore, easily worked by hand under a 'float' and consolidated into a dense, waterproof surfacing.

A large amount of the 'mastic' work, both at home and abroad, is now done with mixtures containing no native rock asphalt, but which are prepared by mixing asphalts with stone dust, crushed rock, sand, or gravel in suitable proportions to yield a waterproof or acid-proof floor or tank lining. Many of the large concrete leaching tanks employed in refining copper as well as concrete pipes and structures exposed to acid in many different industries have been lined or covered with such acid-proof mastic.

For street-paving purposes a selection of one or more rocks are pulverized and blended in suitable proportions to yield an average composition and the physical characteristics desired. Using the European asphalts, the pulverized material is then heated and while hot is spread over a rigid foundation and compressed, usually by hand tamping. The tamped surface may then be smoothed with a light roller. Most American rock asphalts usually contain more bitumen than the European and, consequently, do not have to be heated prior to laying. The rock is crushed and blended to yield a product of average composition with respect to bitumen content. The mixture is laid upon road surfaces, over a more or less rigid foundation, at atmospheric summer temperatures or after warming with live steam if the material is too cool to properly stick together. After spreading the crushed rock upon the road with rakes the surface is then compressed with a power-driven road roller and otherwise manipulated to produce the desired surface.

Specifications.

A specification for limestone rock asphalt is quoted below. This is taken from British Standard Specification for Mastic Asphalt Surfacing, No. 596, 1935, p. 11.

> 'The aggregate shall consist of natural asphalt rock, this term being interpreted in a strictly geological sense and denoting a naturally occurring, consolidated, calcareous rock impregnated with bitumen exclusively by a natural process; the term shall exclude all other types of rock such as result from sporadic bitumen in any mode of occurrence in non-bituminous limestone or in a limestone of low grade impregnation, non-bituminous limestones and artificial mixtures thereof with bitumen of any source and description.
>
> 'The asphalt rock shall be imported in its raw state as mined, so as to be available to the Engineer for sampling and testing, and shall conform to the following specification:
>
> '(i) It shall contain not less than 6% of inherent bitumen.
>
> '(ii) Its specific gravity shall be not less than 1·9 nor more than 2·5.
>
> '(iii) The limestone, after extraction of the bitumen, shall contain not less than 90% of calcium carbonate.
>
> 'The asphalt rock shall be ground to a powder such that the whole shall pass an 8-mesh sieve and at least 15% shall pass a 200-mesh sieve.'

Another specification for limestone rock asphalt is quoted from the General Specification of the Texas (U.S.A.) Highway Department, dated August 1934, 434–53, Sheet No. 1.

> '*Limestone Rock Asphalt.* The limestone rock asphalt shall be uniform, well graded, natural limestone rock asphalt consisting of 9–12% of asphalt and 88–91% of limestone practically free from sulphates, iron pyrites, alumina, or other objectionable matter.'

A typical specification for a sandstone rock asphalt and for a processed rock asphalt taken from page 375 of *Standard Specifications for Road Construction*, State Highway Commission of Indiana (U.S.A.), March 1935, is given below.

'*Rock Asphalt.* The rock asphalt shall be produced from natural bituminous sandstone containing only bitumen native to the rock. It shall be free from clay or other foreign substances. All particles of rock asphalt shall be uniformly coated with bitumen. The rock asphalt shall meet the following requirements:

'1. The sand in the rock asphalt shall be composed of not less than 93% silica.

'2. It shall be thoroughly ground and when tested with sieves having square openings shall comply with the following:

> 'All material shall pass through a 1-in. sieve.
> 'Not over 1% shall be retained on a ¾-in. sieve.
> 'Not over 5% shall be retained on a ½-in. sieve.
> 'Not over 20% shall be retained on a ¼-in. sieve.

'3. The percentage loss on ignition shall be determined on not less than three samples taken from each car. The average of these percentages shall not be less than 6·9% nor more than 7·8%. The variation between the high and low tests shall not exceed 0·75%.

'4. The bitumen by extraction shall not be less than 5·9% nor more than 7·5%.

'*Processed Rock Asphalt.* This material shall consist of a sandstone rock which has been naturally impregnated, by the forces of nature, with bitumen, but with which it is desirable to mix, by artificial methods, such proportions of asphaltic cement as are required to produce a material conforming with the provisions of this specification. It shall be composed of durable angular particles of sand uniformly coated with bitumen. It shall contain, after processing, not less than six and five-tenths (6·5) per cent. nor more than ten and five-tenths (10·5) per cent. of bitumen by extraction. Sandstone aggregate shall contain, after ignition, not less than eighty-eight (88) per cent. of silica (SiO_2) and the per cent. of bitumen by ignition shall be not less than seven (7) per cent. nor more than eleven (11) per cent. For any given material the total variation between these limits shall be as authorized by the Engineer but normally shall be not greater than two (2) per cent. The variation in any sample between the high and low tests shall not exceed one (1) per cent.'

Gilsonite

Gilsonite, originally known as Uintahite or Uintaite, was first discovered by early settlers in the Uintah Valley near Fort Duchesne, Utah, about 1862. W. P. Blake first described the mineral in 1885. The name Gilsonite was adopted because S. H. Gilson, a prospector of Salt Lake City, Utah, first brought it into prominence as an article of commerce.

Gilsonite is found in only one region, being confined to the Uintah Basin in Utah and Colorado. The veins extend from Myton, across Eastern Utah, and for a few miles into Colorado, a total distance of about 60 miles.

The mineral occurs in almost vertical veins, the side walls of which vary in composition from sandstone to shale and invariably run in a general north-west–south-east direction. They vary in width from a fraction of an inch to 18 ft. Some of the longest veins have been traced by outcroppings for a distance of 25 miles. The depth varies from a few to over 700 ft. While usually continuous, the veins are frequently interrupted by faults in the rock structure.

Gilsonite appears to have been derived from rich oil shales which underlay the formations in which the mineral is found. Earth movements tilted the structures and opened fissures in the formations in which the Gilsonite veins occur. Vast erosion has taken place exposing all of these formations. How the fissures were actually filled and how the Gilsonite reached its present state of metamorphosis is uncertain. Some investigators think oil may have been forced under pressure from the oil shales into the fissures in a liquid condition, and that the Gilsonite reached its present state by polymerization and the migration of light fractions into the surrounding rock without the aid of heat over a long period of time. Others claim heat and pressure caused the oil to migrate from the shale into the fissures and only heat could have converted it into Gilsonite. It is a significant fact that the wall rock is often saturated on each side of the vein from a few inches to several feet but dry in all other places, thus showing that the Gilsonite was at one time either a liquid, or a solid or semi-solid liquefied by heat.

As mined, the Gilsonite is graded and packed into burlap sacks, averaging about 200 lb., and either trucked to the nearest shipping-point or carried on the narrow-gauge, tortuous, and scenic Uintah Railroad with its 7½% gradients and 66° curves to its junction with the main railroad at Mack, Colorado.

Gilsonite is one of the purest native bitumens known and is rather readily distinguished from the other asphaltites by its brown streak, lower specific gravity, fixed carbon, and typical low sulphur content.

The Gilsonite mined from different veins varies in characteristics, and while, in general, material taken from a single vein will run fairly uniform, there is some variation from the surface ore which has been altered by the weather to the ore obtained deeper in the shafts. In some veins a variation in fracture of the ore occurs across the vein, frequently being pencillated or columnar at or near the side walls and merging into conchoidal or hackley near the centre. Infrequently ore which is conchoidal when freshly mined gradually becomes hackley. That is, a lump showing entirely conchoidal surfaces will, on ageing, retain this appearance, but the face of a fresh fracture may be entirely hackley or show a hackley area at the periphery and a conchoidal centre. This is entirely a physical or structural phenomenon—none of the other properties are affected.

In general, Gilsonite will be found to comply with the characteristics given in Table XXI.

Some typical analyses of Gilsonite are shown in Table XXII.

TABLE XXI

Gilsonite

Colour in mass	Black
Fracture	Variable, conchoidal, hackley, columnar
Lustre	Coin-like, dull to bright
Streak	Brown
Specific gravity at 60° F.	1·03–1·09
Hardness, Moh's scale	2
Softening-point over mercury	250° F. to over 500° F.
Fixed carbon	10–20%
Bitumen (soluble in CS_2)	Greater than 98·0%
Mineral matter	Less than 1·0%
Non-mineral matter insoluble	Less than 1·0%
Bitumen soluble in 86° naphtha	10–60%
Paraffin scale	Trace
Sulphur	Less than 0·8%

For commercial purposes, Gilsonite is graded into 'Selects' and 'Standard' grades by the larger producers. The differentiation is made primarily on the basis of softening-point and behaviour in petroleum solvents. Formerly the basis of grading was entirely by appearance, principally fracture, the Selects being conchoidal and the Standard otherwise. This, however, proved to be an improper means of classification. In general, Selects and Standard comply with the following:

	Selects	*Standard*
Specific gravity at 60° F., maximum	1·05	1·09
Softening-point over mercury	325° F., max.	. .
Behaviour in petroleum solvent	Does not liver or jell	May liver or jell

In determining the softening-point of Gilsonite, as well as other asphaltites and high softening-point asphalts, a method which does not involve a preliminary melting is to be preferred over any other method. The over-mercury method referred to in Table XXII consists of placing particles of the original material, passing a No. 20 sieve and retained on a No. 30 sieve, on a microscope cover-glass floated on mercury in a 3-oz. tin. An inverted watch-glass with a hole through the centre for a thermometer is used to protect from draughts and the temperature raised at a rate of 10–15° F. (5–6° C.) per minute. The softening-point by this method is defined as the temperature at which all sharp edges and other lines or marks which defined the original shape of the particle round out and disappear when viewed under a magnification of 6 times. At this point the particle is more or less globular. This method eliminates the possibility of altering the softening-point by preliminary melting which may cause a high result if any of the more volatile portions are driven off, or a low result if any cracking or decomposition occurs during the melting pro-

TABLE XXII

Typical Gilsonite Analyses

	'Selects'				*'Standard'*			
	1	*2*	*3*	*4*	*5*	*6*	*7*	*8*
Fracture	Conch.	Conch.	Pencillated	Hackley	Conch.	Conch.	Hackley	Hackley, coin-like
Streak	brown	brown	brown	brown	brown	brown	brown	brown
Specific gravity at 60° F.	1·032	1·044	1·038	1·037	1·051	1·059	1·073	1·069
Softening-point over mercury	265° F.	288° F.	295° F.	315° F.	350° F.	370° F.	465° F.	Over 500° F.
Bitumen soluble in CS_2	99·8%	99·7%	99·7%	99·9%	99·8%	99·5%	99·7%	99·5%
Mineral matter	0·1%	0·2%	0·2%	0·1%	0·1%	0·3%	0·2%	0·3%
Difference	0·1%	0·1%	0·1%	trace	0·1%	0·2%	0·1%	0·2%
Bitumen soluble in 86° naphtha	51·5%	49·5%	42·6%	43·3%	21·7%	21·0%	11·1%	12·4%
Fixed carbon	14·5%	15·1%	13·7%	14·7%	17·9%	20·9%	18·9%	15·1%
Sulphur	0·2%	0·3%	0·5%	0·4%	0·3%	0·6%	0·3%	0·4%
Behaviour in petroleum solvent	liquid	liquid	liquid	liquid	thickens and jells			

cess. For this reason, the over-mercury method is to be preferred to any other involving a preliminary melting.

The behaviour in petroleum solvents is determined by combining under reflux about 70 parts solvent and 30 parts ore by weight, allowing to cool and noting whether a permanently liquid mixture or one that either jells immediately or on standing is obtained. Frequently an actual viscosity is determined when the type of solvent is well standardized.

Gilsonite is miscible in all proportions with the drying oils and resins generally employed in the manufacture of oleo-resin varnishes, and is miscible with all petroleum residuals and other asphalts, and when compounded with them is widely used in the manufacture of various black varnishes and baking japans.

Gilsonite is widely employed in the manufacture of storage battery cases and other thermo-plastic moulded articles, brake linings, mastic flooring, asphalt tile, battery-sealing compounds, saturating compounds for insulated wire, belting, various impregnated fabrics, wood stains, pipeline coatings, and many other varieties of compounds. Because of its brown undertone, Gilsonite is used widely in printing-inks, especially the brown rotogravure types.

A high dielectric strength is a characteristic of Gilsonite which is responsible for its use in many electrical compounds.

Gilsonite is vitally different from almost all other petroleum or native asphalts in its ability to mix in almost any proportion with waxes to form stable compounds, whereas only limited proportions of waxes can be incorporated in other asphalts to form stable compounds. It is frequently used in small proportions in wax-asphalt mixtures where it acts as a blender or carrier and prevents the separation of wax and asphalt. The greasiness or oiliness of some blown or oxidized asphalts may be decreased by adding a small percentage of Gilsonite either to the flux before blowing or to the finished blown asphalt.

Gilsonite added to a high softening-point oxidized asphalt reduces both penetration and softening-point, but when added to a low softening-point oxidized asphalt reduces penetration but elevates softening-point.

Grahamite

Grahamite, an asphaltite, occurs in several localities in the United States as well as in Cuba and South America. It was discovered in 1863 by J. P. Leslie in West Virginia and named in honour of Messrs. J. A. and J. L. Graham, who were largely interested in the West Virginia mine.

Deposits in Oklahoma were exploited to a very considerable extent for a number of years, but practically all of the Grahamite in commercial quantities at the present time is taken from the mines in Cuba, but even this has but limited use.

Two deposits of Grahamite which occur in Trinidad, B.W.I., near San Fernando on the west coast of the island on the shore of the Gulf of Paria, are known as the Vistabella and the Marbella Mines. This material has been referred to as Manjak, but is actually Grahamite. A number of veins have been uncovered, the largest of which, known as the Vistabella Mine, measures 360 ft. horizontally and has been mined to a depth of 260 ft. Its thickness is 11 ft. at the top and increases steadily to 33 ft. at a depth of 200 ft.

Grahamite is sharply differentiated from Gilsonite and Glance Pitch by its higher fixed carbon and the fact that it intumesces but does not melt upon the application of heat. The colour of its streak and powder is decidedly blacker than that of either Gilsonite or Glance Pitch.

Grahamite varies considerably in composition and physical properties, some deposits occurring fairly pure, whereas others are associated with mineral matter, running as high as 50%. In general, however, it complies with the analysis given in Table XXIII, which is taken from Abraham [1, 1929].

TABLE XXIII

Grahamite

Colour in mass	Black
Fracture	Conchoidal to hackley
Lustre	Very bright to dull
Streak on porcelain	Black
Specific gravity at 77° F.:	
Pure varieties (containing less than 10% mineral matter)	1·15–1·20
Impure varieties (containing more than 10% mineral matter)	1·175–1·50
Hardness, Moh's scale	2–3
„ needle penetrometer at 77° F.	0
„ consistometer at 77° F.	Over 150
Susceptibility factor	> 100
Behaviour on heating in flame:	
Variety showing a conchoidal fracture and a black lustre	Decrepitates violently
Variety showing a hackley fracture and a fairly bright to dull lustre	Softens, splits, burns
Fusing-point (K. and S. method)	350–600° F.
„ (Ring and Ball method)	370–625° F.
Volatile at 500° F., 5 hr.	Less than 1%
Fixed carbon	30–55%
Soluble in carbon disulphide	45–100%
Non-mineral matter insoluble in CS_2	Less than 5%
Mineral matter	Variable (up to 50%)
Carbenes	0·80%
Soluble in 88° petroleum naphtha	Trace–50%
Oxygen in non-mineral matter	0–2%
Solid paraffins	0–trace %
Sulphonation residue	80–95%
Saponifiable matter	Trace
Diazo reaction	None
Anthraquinone reaction	None

Grahamites from West Virginia and Oklahoma have been analysed by Richardson [10, 1908], who gives the results shown in Table XXIV.

TABLE XXIV

Grahamite

	Oklahoma	West Virginia
Physical properties		
Specific gravity, 78° F./78° F., original substance, dry	1·171	1·137
Colour of powder or streak	Black	Black
Lustre	Dull	Dull
Structure	Uniform	Uniform, friable
Fracture	Hackley	Irregular
Hardness, original substance	Brittle	2
Odour	None	None
Softens	Intumesces	Intumesces
Flows	Intumesces	Intumesces
Penetration at 78° F.	0	0
Chemical properties		
Dry substance:		
Loss, 325° F., 7 hr.	+0·1%	..
Loss 400° F., 7 hr. (fresh sample)	+0·5%	..
Bitumen soluble in CS_2, air temperature	94·1%	97·8%
Difference	0·2%	0·1%
Inorganic or mineral matter	5·1%	2·1%
	100·0%	100·0%

TABLE XXIV (*cont.*)

	Oklahoma	*West Virginia*
Chemical properties		
Malthenes:		
Bitumen soluble in 88° naphtha, air temperature	0·4%	3·3%
This is per cent. of total bitumen	0·4	3·37
Per cent. of soluble bitumen removed by sulphuric acid	25·0	..
Per cent. of total bitumen saturated hydrocarbons	0·32	..
Bitumen soluble in 62° naphtha	0·7%	3·4%
This is per cent. of total bitumen	0·7	3·47
Carbenes:		
Bitumen insoluble in carbon tetrachloride, air temperature	68·7%	55·0%
Bitumen insoluble in hot carbon tetrachloride	48·6%	1·3%
Bitumen yields on ignition:		
Fixed carbon	53·3%	41·0%
Ultimate composition:		
Carbon	..	86·56%
Hydrogen	..	8·68%
Sulphur	..	1·79%
Difference	..	2·97%
		100·00%

Grahamite is found in several localities on the Island of Cuba, especially in the provinces of Pinar del Rio and Santa Clara. Under Cuban Asphalts below will be found analyses of materials taken from the Ana Maria and La Esperanza deposits which probably are typical of Cuban Grahamite.

TABLE XXV

Grahamite from Vistabella Mine in Trinidad

Colour in mass	Black
Homogeneity	3 distinct types recognizable
Fracture	Types 1 and 2, hackley; type 3, conchoidal.
Lustre	Types 1 and 2 dull; type 3 bright.
Streak	Black
Specific gravity, at 77° F.	1·170–1·175
Hardness, Moh's scale	2
„ penetrometer	0
On heating in flame	Softens, splits, and burns
Fusing-point (K. and S. method)	350–438° F.
„ (R. and B. method)	370–460° F.
Fixed carbon	31·5–35·0%
Solubility in carbon disulphide	91·7–96·0%
Non-mineral matter insoluble	0·9–1·2%
Free mineral matter	4·0–6·4, averaging about 5·7%
Mineral matter combined with non-mineral constituents	1·15%
Carbenes	About 40%
Solubility in 88° petroleum naphtha:	
At 100-ft. level	12·8%
At 140-ft. level	15·2%
At 200-ft. level	18·5%
At 200-ft. level, softer material in centre	56·0%
Moisture	0·2–1·0%
Carbon	84·0%
Hydrogen	5·7%
Sulphur	3·0–3·8%
Nitrogen	2·2%

Note: The material resembling glance pitch obtained from the centre of the vein at the 200-ft. level fused at 280° F. (K. and S. method).

Abraham's [1, 1929] analysis of Grahamite from the Vistabella Mine on the Island of Trinidad is given in Table XXV.

Two deposits of hard asphaltite are found in Mexico near the town of Papantla in the State of Vera Cruz, which, although they have some of the characteristics of Gilsonite, cannot be so classified because of the high fixed carbon content, low per cent. soluble in ethyl ether, and frequent absence of a definite softening-point.

One of the deposits is known as Papantla after the nearby town, and the other is called Espinal. Analyses of samples taken from these deposits are given in Table XXVI.

TABLE XXVI

Mexican Grahamite

	Papantla	*Espinal*
Character of fracture	Conchoidal	Conchoidal
Colour of streak	Black	Black
Odour on heating	Asphaltic	Asphaltic
Specific gravity at 60° F.	1·113	1·145
Softening-point over mercury	286° F.	Over 500° F.
Bitumen soluble in CS_2	99·12%	99·22%
Mineral matter	0·62%	0·58%
Difference	0·26%	0·20%
Bitumen soluble in ethyl ether	40·98%	19·45%
„ „ 86° naphtha	30·37%	9·22%
Fixed carbon	23·00%	35·90%
Sulphur	8·42%	6·91%

Several deposits of Grahamite are known in the Republic of the Argentine. In Mendoza Province there occurs an asphaltite which is probably a Grahamite. The ash from this material carries almost 40% vanadium oxide.

A peculiar type of Grahamite occurs in Neuquen Province on the eastern slope of the Andes Mountains. Abraham [1, 1929] describes the material as follows and gives the analysis shown in Table XXVII.

TABLE XXVII

Grahamite from Neuquen Province, Argentine

Colour in mass	Black
Fracture	Conchoidal
Lustre	Bright
Streak	Black
Specific gravity at 77° F.	1·135
Fusing-point (K. and S. method)	About 625° F.
Behaviour on heating in flame	Decrepitates violently
Soluble in carbon disulphide	53·35%
Non-mineral matter insoluble	46·40%
Mineral matter	0·25%
	100·00%

'This asphaltite fluxes with great difficulty with residual oils derived from asphaltic and semi-asphaltic petroleums, which necessitates the mixture being heated to 500° F. for several hours. During this treatment the "non-mineral matter insoluble" undergoes depolymerization until it all eventually goes into solution. On the other hand, it fluxes quite readily with linseed oil on heating to 500° F. This Grahamite is unusual, in that although half is insoluble in carbon disulphide, yet it may be fluxed completely as described. It is apparently on the border-line between true Grahamite and Impsonite.'

A number of deposits of asphaltite are also found in Neuquen Province, Argentine, which are produced under the name of 'Rafaelite'. From the data given in Table XXVIII it will be noted that the properties of these materials approach those of certain grades of Gilsonite except as to specific gravity, sulphur, and fixed carbon content.

TABLE XXVIII

Rafaelite from Argentine

Specific gravity	1·099–1·103
Softening-point (over mercury)	380° F.–over 400° F.
Bitumen (soluble in CS_2)	98·7–99·7 %
Mineral matter	0·4–0·0 %
Difference	0·9–0·3 %
Fixed carbon	29·6–29·8 %
Streak on porcelain	Brownish-black to black
Bitumen soluble in 86° naphtha	33·6–35·2 %
Bitumen soluble in ethyl ether	41·2–42·5 %
Sulphur	2·2–2·9 %

No extensive use of Grahamite has been made in recent years. Formerly the pure variety from Oklahoma was widely employed, after blending it with petroleum residuum, in the production of compounds possessing a rubbery nature. These compounds were used for pipe coating, for roofing felts, as waterproofing material, and for filling expansion joints in rigid types of paving construction and concrete structures.

Some varieties from Cuba when mixed with other asphalts have been used at various times for street- and road-paving purposes.

While Grahamite does not melt when heated alone, it can be fluxed with certain types of petroleum residuum at temperatures around 500° F. Such treatment softens and modifies it into a rubbery compound. Mixtures so prepared are soluble in the usual complete solvents for bitumen, but may be expected to 'liver' badly in petroleum naphtha. These characteristics resemble very closely those of oxidized petroleum asphalts by which the fluxed Grahamites have been quite generally superseded.

Cuban Asphalts

A variety of native asphalts, which range in characteristics from the Grahamitic to the Gilsonitic types, occurs widely distributed over the Island of Cuba. In those of the latter type the sulphur and fixed carbon content and specific gravity are almost invariably higher, while the bitumen content is generally lower than for Gilsonite from other localities.

Although the deposits are numerous and cover a wide area, they do not seem to exist in definite vein formation but rather in disconnected pockets. Some of the deposits are actually mined from beneath the sea.

Data concerning the properties of asphalts from nine different Cuban deposits are given in Table XXIX.

Glance Pitch

An asphaltite, known as Glance Pitch and marketed under the name of 'Manjak', was first reported on the Island of Barbadoes in 1750. The name 'Manjak' was later also used to designate Grahamite obtained in Trinidad. Barbadoes glance pitch varies in characteristics from the top to the bottom of the deposits, being hard and brittle at the top and quite soft at the bottom. Table XXX gives an analysis of this material which was made by Richardson [10, 1908].

A deposit of glance pitch of commercial importance is found about 100 miles south-west of Bogota in the State of Tolima, Republic of Colombia. Abraham [1, 1929] gives the analysis shown in Table XXXI

TABLE XXIX

Cuban Asphaltites

Province	Santa Clara	Santa Clara	Santa Clara	Camaguey
Mine	6th de Febrero	La Esperanza	La Esperanza	Coto San Marcos
Year	1934	1934	1934	1934
Character of fracture	Hackley	Conch.	Conch.	Hackley
Colour of streak	Dark brown	Dark brown	Black	Black
Softening-point over mercury	401° F.	Over 500° F.	324° F.	424° F.
Specific gravity at 60° F.	1·162	1·172	1·140	1·138
Soluble in CS_2	98·5 %	98·1 %	98·2 %	97·0 %
Mineral matter (ash)	1·3 %	1·3 %	1·4 %	2·4 %
Difference	0·2 %	0·6 %	0·4 %	0·6 %
% bitumen soluble				
in CCl_4	99·8 %	..	99·4 %	99·8 %
in ethyl ether	22·4 %	29·0 %	33·0 %	19·1 %
in 86° naphtha	14·1 %	22·3 %	22·6 %	9·5 %
Fixed carbon	30·7 %	41·0 %	24·1 %	31·2 %
Sulphur	8·9 %	6·2 %	9·3 %	8·2 %
Hardening power (parts by weight):				
Sample	100	100	100	100
Asphalt of 10 pen. at 77° F.	150	212	50	170
Mixture softening-point (R. and B.)	248° F.	247° F.	252° F.	248° F.
Penetration 115° F., 200 g., 5 sec.	9	12	10	8

Province	Santa Clara	Santa Clara	Pinar del Rio	Matanzas	Pinar del Rio
Mine	Santa Eloisa	Ana Maria	Santa Julia	Bahia de Cardenas	San Juan Bautista (Mariel)
Year	1934	1934	1934	1934	1934
Character of fracture	Hackley	Hackley	Laminar to conch.	Conch.	Hackley
Colour of streak	Dark brown	Dark brown	Dark brown to black	Black	Dark brown
Softening-point over mercury	376° F.	Over 500° F.	435° F.	296° F.	355° F.
Specific gravity at 60° F.	1·291	1·172	1·160	1·169	1·577
Soluble in CS_2	77·0 %	98·7 %	99·1 %	94·6 %	54·0 %
Mineral matter (ash)	20·6 %	0·8 %	0·6 %	4·4 %	40·8 %
Difference	2·4 %	0·5 %	0·3 %	1·0 %	5·2 %
% bitumen soluble:					
in CCl_4	99·8 %	..	99·3 %	99·8 %	99·8 %
in ethyl ether	37·0 %	25·5 %	30·0 %	32·4 %	43·8 %
in 86° naphtha	27·0 %	10·0 %	21·3 %	25·2 %	38·0 %
Fixed carbon	31·2 %	40·3 %	37·1 %	26·1 %	26·3 %
Sulphur	6·7 %	6·8 %	7·9 %	10·0 %	6·1 %
Hardening power (parts by weight):					
Sample	..	100	100	100	..
Asphalt of 10 pen. at 77° F.	..	338	163	64	..
Mixture softening-point (R. and B.)	..	248° F.	251° F.	247° F.	..
Penetration 115° F., 200 g., 5 sec.	..	12	10	8	..

TABLE XXX

Glance Pitch (Manjak) from Barbadoes

Physical properties

Specific gravity, 78° F./78° F., original substance, dry	1·0844
Colour of powder or streak	Dark brown
Lustre	Lustrous
Structure	Uniform
Fracture	Conchoidal
Hardness, original substance	1
Softens	230° F.
Flows	250° F.
Penetration at 78° F.	0°

Table XXX (*cont.*)

Chemical Characteristics

Bitumen soluble in CS_2, air temperature	99·2%
Difference	0·5%
Inorganic or mineral matter	0·3%
	100·0%
Malthenes:	
Bitumen soluble in 88° naphtha, air temperature	26·9%
This is per cent. of soluble bitumen	27·0
Per cent. of soluble bitumen removed by H_2SO_4	75·0
Bitumen soluble in 62° naphtha	40·4%
This is per cent. of total bitumen	40·7
Carbenes:	
Bitumen insoluble in carbon tetrachloride, air temperature	1·2%
Bitumen yields on ignition:	
Fixed carbon	25·0%

Glance pitch is intermediate between Gilsonite and Grahamite. It has a higher specific gravity and melting-point, and the colour of its streak and powder is blacker than Gilsonite. It is also more difficultly fusible, less soluble in petroleum naphtha, and has a greater tendency to 'liver' in naphtha solution.

Table XXXI

Glance Pitch from Colombia

Fracture	Conchoidal
Lustre	Bright
Streak	Black
Specific gravity at 77° F.	1·12
Hardness, Moh's scale	2
„ penetrometer	0
Fusing-point (K. and S. method)	275° F.
Fixed carbon	26·45%
Solubility in carbon disulphide	96·0%
Non-mineral matter insoluble	0·7%
Mineral matter	3·3%

Several varieties of glance pitch have been marketed for many years, the Barbadoes (Manjak) enjoying more or less favour in the manufacture of black varnishes and japans on account of its gloss and intense black colour.

Supplies from Cuba are quite variable as the production there from any single vein is relatively small, is not well organized, and has been derived from several deposits without regard to any special standard of quality. It is sometimes offered as a substitute for Gilsonite, from which it differs in several important respects. However, the supply of glance pitch from Cuba is probably better known than that from the West Indies or elsewhere, and is used to some extent, compounded with other bituminous materials, in the manufacture of varnish, thermo-plastics, and other products.

REFERENCES

1. Abraham, Herbert. *Asphalts and Allied Substances*, 3rd ed. D. Van Nostrand Company, New York, N.Y. (1929).
2. Abson, Gene. *Proc. A.S.T.M.* **33**, ii, 704 (1933).
3. Anon. *Contractors' Record and Municipal Engineering*, 5 Feb. (1930).
4. Broome, D. C., and Thomas, A. R. *J.S.C.I.* **50**, 424 T (1931).
5. Kirschbraun, L. *Ind. Eng. Chem.* **6**, 976 (1914).
6. Le Gavrian, P. *Les Chaussées Modernes*, 2nd ed. Paris (1935).
7. Paillar, E. C. *Ind. Eng. Chem.* **6**, 286 (1914).
8. Pittman, C. U., and Traxler, R. N. *Physics*, **5**, 221 (1934).
9. Pochettino, A. *Nuovo cimento*, **8**, 77–108 (1914).
10. Richardson, C. *The Modern Asphalt Pavement*, 2nd ed. John Wiley & Sons, New York (1908).
11. Saal, R. N. J. *Proc. World Petr. Cong.* **2**, 515 (1933).
12. Saal, R. N. J., and Koens, G. *J.I.P.T.* **19**, 176 (1933).
13. Strieter, O. G. *The Mechanism of Asphalt Formation.* Dissertation Columbia University, New York, N.Y. (1925).
14. Sub-Committee X of the American Society for Testing Materials. *Proc. A.S.T.M.* **34**, i, 486 (1934).
15. Traxler, R. N., Pittman, C. U., and Burns, F. B. *Physics*, **6**, 58 (1935).
16. Wichert, P. *Asphalt und Teer.* Strassenbautechnik no. 36 (1929).
17. Wilson, D. M. *Chemistry and Industry*, **53**, 924 (1934).

ASPHALTIC PRODUCTS FOR PAVEMENTS AND HIGHWAYS

By PREVOST HUBBARD

Past President of the Association of Asphalt Paving Technologists

Classification and Production

THROUGHOUT this article attention is called to the use of the term asphalt according to American nomenclature as distinct from European. In the United States the term asphalt is confined to solid or semisolid products in which the predominating constituents are bitumens. While petroleum residua and native products, such as Trinidad asphalt, are thus classed as asphalts, bituminous rock is not included under the term. According to the British and European definition, mineral matter is a necessary constituent of asphalt, and the term includes bituminous rock, but eliminates semisolid and solid petroleum residua to which the term asphaltic bitumen is applied.

Asphaltic products are extensively used in highway construction and maintenance because of their cementitious and waterproof characteristics, their durability or resistance to the destructive action of traffic and weather, and their ability to impart a certain degree of flexibility to the road structure. Asphaltic highway materials commonly manufactured and marketed by petroleum refiners are shown in the following tabulation, together with other native asphaltic materials which are not a direct product of petroleum refining, but are also used for highway purposes.

I. *Solids and Semisolids.*
  1. Hard, brittle asphalts (which may be used in pulverized form):
    (*a*) Refined from petroleum.
    (*b*) Refined native asphalts such as Trinidad and Cuban.
  2. Asphalt cements:
    (*a*) Semisolid asphalts refined from petroleum.
    (*b*) Fluxed native asphalts.

II. *Liquids.*
  1. Residuals from petroleum refining:
    (*a*) For direct use as highway materials.
    (*b*) For fluxing hard asphalts so as to produce asphalt cements of any desired consistency.
  2. Viscous petroleum residuals blended with gas-oil distillates to produce products of lower viscosity.
  3. Cut-back asphalts—asphalt cements fluxed with volatile petroleum distillates.
  *4. Asphalt emulsions:
    (*a*) Emulsions of asphalt cements with water.
    (*b*) Emulsions of liquid petroleum residuals with water.

In addition to those listed, native asphaltic materials, known as bituminous rock or rock asphalts, are also used for highway purposes. These products, which consist predominatingly of mineral matter, such as sandstone or limestone, should, however, be considered in comparison with paving compositions produced by admixture of the other asphaltic materials with mineral aggregates.

The highway industry consumes the greater part of all asphaltic materials produced. Manufacture of such products from petroleum has developed much more extensively in the United States than in all other countries combined. Accurate world production statistics are difficult to secure, but for 1932 it would appear that the United States can be credited with about 75% of the total production from petroleum.

For a number of years past the U.S. Bureau of Mines has collected and published records of the production and sale of asphaltic products, according to use by petroleum refineries in the United States. Table I shows such total production for the years 1925 to 1934 inclusive, with the quantity and percentage used for highways.

TABLE I

Production and Sale of Asphaltic Material from Petroleum in the United States

Year	*Total, short tons**	*Total for highways, short tons*	*For highways, % of total*
1925	3,079,371	1,764,700	55·6
1926	3,178,370	1,800,180	52·1
1927	3,458,470	2,179,100	55·2
1928	3,951,450	2,487,642	55·2
1929	4,229,384	2,655,989	56·7
1930	4,688,471	2,693,552	64·8
1931	4,153,994	2,901,851	71·3
1932	4,073,870	2,838,344	74·8
1933	3,797,864	2,500,110	72·0
1934	4,011,033	2,977,990	74·2

* Of 2,000 lb.

Table II shows the production and sale of asphaltic products at petroleum refineries for 1934, classified according to use. In this table the cut-back asphalt and emulsified asphalt has been credited to highway uses. The great bulk of these products is used for such purposes, although no detailed statistics are available for classifying them. An appreciable amount of paving asphalt and flux is sold by the petroleum refiners to companies manufacturing emulsions. It is estimated that the actual total of emulsified asphalts for 1934 was, therefore, 168,000 tons.

During 1934, 15,679 short tons of native asphalt, valued at $222,372, were imported by the United States, a considerable portion of which was used for highway purposes. In addition, 410,453 tons of rock asphalt, valued at $1,762,376, were mined and sold in the United States mainly for highway construction and maintenance.

Highway Uses for Asphalt

There are various types of pavement and highway in which asphaltic products are used and various methods of construction or application, all of which have an important relation to the characteristics which the asphaltic material should possess. Highway structures in which asphalt serves as the principal cementing medium are known as asphalt roads and pavements. Where the structure consists of two or more courses asphalt may be used in any or all of the courses. The term asphalt pavement is usually applied to any highway structure which has a wearing course of over

---

* Asphalt emulsions are fully covered in another contribution, and their characteristics and uses are therefore not described in detail in this article.

TABLE II

Production and Sale of Asphaltic Materials at Petroleum Refineries, 1934

Use	*Short tons*	*Value*
Pavements and highways:		$
Asphalt cements	924,135	9,950,192
Fluxes	113,362	1,153,387
Cut-back asphalts	624,183	7,525,165
Emulsified asphalts	32,518	496,774
Road oils	1,283,792	10,741,998
Total	2,977,990	29,867,516
Roofing	751,790	7,483,062
Waterproofing	110,838	1,239,625
Mineral rubber	16,606	314,339
Briquetting	37,544	412,703
Mastic	1,155	12,848
Pipe coatings	7,342	107,532
Paints, enamels, japans, &c.	14,179	193,336
Moulding compositions	11,120	136,344
Miscellaneous	82,469	867,637
Grand Total	4,011,033	40,634,942

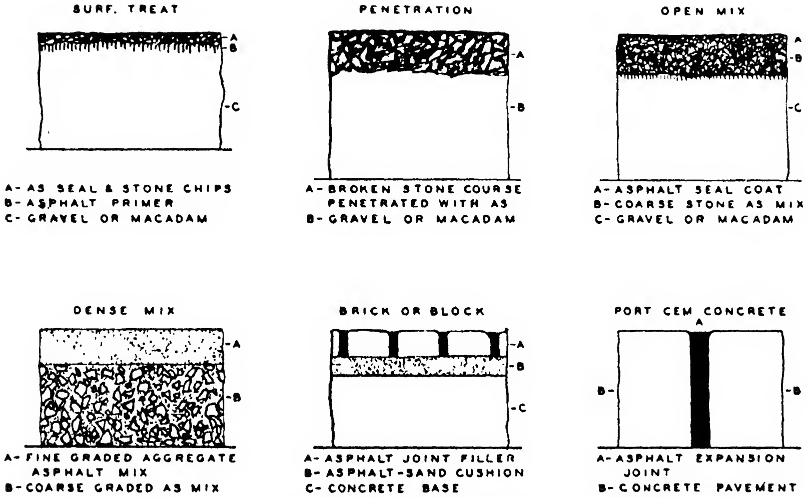


FIG. 1. Pavement cross-sections showing use of asphalts.

¾ in. thickness, the aggregate of which is bound together with asphalt. Where the wearing course is less than ¾ in. thick, it is usually called a surface treatment. Asphaltic products are also used as joint and crack fillers for brick, block, and monolithic pavements. Typical cross-sections of pavements in the construction of which asphalt is used are shown in Fig. 1.

Surface treatments are made by applying liquid residuals, cut-backs, or emulsified asphalts to an existing road surface by means of a pressure distributor. When the object of treatment is merely to lay dust on an earth, gravel, or macadam road a cheap liquid residual of low viscosity and high penetrating properties may be used. Such a product will be largely absorbed by the road surface and may require no cover coat of mineral aggregate. When the treatment is made to produce a thin mat or carpet coat over the road, a cut-back asphalt or very viscous liquid residual is best adapted for use. If the existing road is not of a bituminous type, the surface should first be primed with a liquid asphaltic product of very low viscosity. After application of the mat-forming asphaltic product, the surface is covered with a light dressing of stone chips, pea gravel, or sand which is thus bound to the underlying road.

The penetration type of construction is usually laid as a wearing course of 2 to 3 in. thickness upon a gravel or broken-stone foundation. It is commonly known as asphalt macadam. The mineral aggregate of the wearing course should consist of a rather uniform size commercial broken-stone product with a maximum diameter limited to that of the thickness of the course and a minimum diameter about half its thickness. Such an aggregate, after compaction, contains relatively large uniformly distributed voids, thus permitting the asphalt binder, which is applied to the surface, to penetrate for the full depth and cement the fragments together. A relatively soft asphalt cement is ordinarily used for this purpose and is applied hot by means of a pressure distributor. The surface is then chinked with a smaller broken-stone aggregate and sealed with a light application of hot asphalt cement and mineral cover.

Mixed types of asphalt pavements may be constructed with a great variety of mineral aggregates and asphaltic binders, and the mixtures may be prepared and laid in various ways. The simplest and crudest method of preparing the mixture, widely used in low-cost secondary highway construction, consists in first spreading the loose aggregate over the roadway and applying the asphaltic material by means of a pressure distributor, after which the aggregate and binder are mixed in place on the road by means of grader blades, drags, or special road-mixing equipment. The method used in high-type pavement construction is known as plant mix. It most frequently involves heating and drying the mineral aggregate as well as the asphaltic binder, after which the two are combined in predetermined proportions and thoroughly mixed in a mechanical mixer before being placed and compacted on the road. Some mixtures can only be placed and compacted while hot, while others are designed to be laid cold.

Open-type mixtures are prepared with a mineral aggregate in which, after compaction, there is a high percentage of relatively large voids, a condition somewhat like that of the asphalt macadam. In such mixtures the mineral aggregate should consist of relatively coarse angular fragments which interlock under compression so as to produce high structural strength. A commercial broken-stone product is most commonly used, but the maximum diameter is usually limited to 1¼ or 1½ in. It has been found essential to coat such an aggregate with as thick a film of asphalt as it can carry in the loose state without loss due to drainage from the surfaces. In road-mix construction, such films are secured by use of a low viscosity cut-back asphalt containing a very volatile distillate. For plant-mix construction a similar type of cut-back of higher viscosity is used, or else the dry but not hot aggregate is first sprayed with a volatile distillate, after which it may be mixed with a relatively soft asphalt cement and the mixture laid cold. Preheating the coarse high-void aggregate to a temperature sufficiently high for it to be mixed directly with an asphalt cement will not permit it to retain a sufficiently thick film to produce a durable paving mixture. The surface of all open-type mixtures after compaction as a wearing course should be sealed by suitable means, as in the case of asphalt macadam.

Close-type mixtures are prepared with mineral aggregates so graded from coarse to fine that after compaction the voids are low in quantity and small in size. Such aggregates will carry a sufficiently high percentage of asphalt to produce dense waterproof mixtures when compacted. The maximum size of particle in the graded aggregate should always be less than the thickness of the compacted course of pavement, and in some types of mixtures is less than ⅛-in. diameter. For road-mix construction it is desirable that the aggregate contain a substantial proportion of broken stone or gravel coarser than sand. A special type of cut-back asphalt is best adapted to produce a road mix, although liquid residuals are often used. For cold-laid plant mix with such aggregates the same types of asphaltic products, but of somewhat higher viscosity, are used. Hard, powdered asphalt may often be advantageously incorporated in mixtures produced with liquid residuals. For hot-laid plant-mix construction the preheated aggregate is combined directly with hot asphalt cement. When the mixture contains an appreciable proportion of mineral particles coarser than sand, it is known as asphaltic concrete. When sand is the coarsest mineral constituent it is known as sheet asphalt. Close-graded hot-mix asphaltic concrete, with maximum-size particle of not over ½ in., is used in the manufacture of block and tile for paving purposes. The hot mixture is moulded under high pressure in specially designed presses, and the finished product is known as asphalt block.

Asphalt is used in a variety of ways to fill and waterproof joints and cracks in brick, block, and monolithic pavements. When the joint spaces are narrow, as in the case of brick, they are often filled directly with hot asphalt cement. For wider joints such as exist in stone block pavements, a mixture composed of approximately equal parts by volume of hot sand and asphalt cement is used, or else a mineral-filled asphalt prepared by the refiner consisting of asphalt cement carrying in suspension a substantial quantity of very finely divided mineral matter. Wide expansion joints which are constructed in monolithic pavements are often filled with preformed joint compositions consisting of oxidized asphalt, mixtures of asphalt with fine mineral aggregate, sawdust, cork, felt or fibrous material, and in some cases reinforced with asphalt saturated fabric. Asphaltic bedding-courses for brick and block pavements consist of mixtures of sand with asphalt cement laid hot or sand mixed with liquid asphaltic products laid cold.

Asphalt Cements

The term asphalt cement as here used is in accord with the standard definition of the American Society for Testing Materials as follows: '*Asphalt Cement.*—A fluxed or unfluxed asphalt specially prepared as to quality and consistency for direct use in the manufacture of bituminous pavements, and having a penetration at 25° C. (77° F.) of between 5 and 250, under a load of 100 g. applied for 5 seconds.' If the product has a lower penetration than 5, it is generally known as hard asphalt, and if its penetration is more than 250, under the stated conditions of temperature, load, and time, but of not more than 350 at 25° C. (77° F.) under a load of 50 g. applied for 1 sec., it is known as soft asphalt.

Asphalt cements are manufactured for use in the paving industry in a number of grades defined by penetration limits. In American practice it has been found satisfactory from the consumers' standpoint to accept asphalt cement of any penetration, coming within the penetration limits set for the particular grade required, although the manufacturer is supposed to produce material as close as practicable to the midpoint of each grade. For asphalt pavement construction the U.S. Bureau of Standards in Simplified Practice Recommendation no. 4 has established the following ten grades, which have been found to meet the great bulk of consumer requirements and have been accepted by the asphalt producers.

Grades of Asphalt Cement for Paving as defined by Penetration Limits

(77° F., 100 g., 5 sec.)

25 to 30
30 to 40
40 to 50
50 to 60
60 to 70
70 to 85
85 to 100
100 to 120
120 to 150
150 to 200

Most of the asphalt cements for paving purposes manufactured to meet these requirements are produced by the direct distillation or reduction of selected crude petroleums. In some cases, however, the petroleum refiner may distil down to a product of lower penetration than that of the particular grade desired and then flux the resultant hard asphalt with a selected non-volatile liquid petroleum residuum or high-boiling distillate. Refined native asphalts are usually so hard that they must be fluxed to bring them within any of the penetration limits set for asphalt cement.

For the manufacture of asphalt block, asphalt cements of 25 to 30 or 30 to 40 penetration are used, and sometimes those running as low as 10 penetration. For hot-mix pavements, grades of 40 to 50 and 50 to 60 penetration are most commonly used in sheet asphalt and other mixtures in which the predominating mineral constituent is sand; and for hot-mix asphaltic concrete, where the predominating mineral constituent is coarser than sand, the 50 to 60 and 60 to 70 penetration grades are in most demand. Softer grades up to 150 penetration are used in the construction of asphalt macadam pavements, and the 150 to 200 penetration grade is sometimes used for surface treatment. For the preparation of cold-laid open-type paving mixtures, when, before mixing, the aggregate is sprayed with a volatile distillate, the 85 to 100 penetration grade is most frequently specified.

The consistency or hardness of an asphalt cement is an important property affecting its suitability for use in the various types of asphalt pavements which have been described. The penetration test at 77° F. has come to be the generally accepted method of rating its consistency, but the importance of the unit of measuring penetration is commonly over-estimated. Consistency, hardness, or penetration of any asphalt cement is a variable depending upon its temperature and products of the same penetration at 77° F. produced from different sources, and by variations in refining processes may show widely different penetrations at other temperatures. Temperature susceptibility is sometimes limited in specifications for certain grades of asphalt cement by a requirement covering maximum permissible penetration at an elevated temperature and minimum permissible penetration at a lower temperature than 77° F. Various methods have been devised for the purpose of evaluating temperature susceptibility on a comparative basis covering all penetration grades of asphalt throughout the temperature range to which they will be subjected under service conditions. This, however, is a difficult matter, due to the wide variations in consistency of such products at maximum and minimum service temperatures and the limitations of all commonly used tests for measuring consistency. This subject will be more fully covered later in this article.

TABLE III

Typical Characteristics of Petroleum Asphalt Paving Cements

40–50 Penetration

Source	*Mex.*	*Venezuelan*	*Columb. Sl. Ox.*	*Mid.-Cont.*	*Calif.*	*Calif. Sl. Ox.*
Sp. gr. 60/60° F.	1·056	1·043	1·020	1·012	1·021	1·020
Flash-pt. ° F., Open Cup	552°	517°	632°	585°	578°	445°
Softening-pt. ° F., Ring and Ball	133°	128°	134°	128°	123°	135°
Furol vis. 300° F.	191	169	203	96	74	137
Pen. 77° F., 100 g., 5 sec.	47	45	40	47	41	41
Pen. 32° F., 200 g., 1 min.	17	15	14	13	7	16
Pen. 115° F., 50 g., 5 sec.	198	217	161	242	Too soft	183
Ductility 77° F.	100+	100+	100+	100+	100+	100+
Loss 325° F., 50 g., 5 hr., %	0·04	0·21	0·02	0·03	0·00	0·19
Pen resid. 77° F., 100 g., 5 sec.	42	37	37	38	38	38
Sol. CS_2, %	99·9	99·8	99·9	99·8	99·9	99·9
Sol. CCl_4, %	99·8	99·8	99·8	99·8	99·8	99·8

TABLE IV

Specifications for Petroleum Asphalt Paving Cements

Specification	*United States Federal Specifications SS. A-706*						*British Standard*
Designation	*AP. 1–25*	*AP. 2–25*	*AP. 3–25*	*AP. 5–25*	*AP. 6–25*	*AP. 7–25*	*As. bitumen*
Sp. gr. 60° F.	..	..	..	..	..	..	1·00–1·06
Sp. gr. 77/77° F.	1·000+	1·000+	1·000+	1·010+	1·010+	1·010+	..
Flash-pt. ° F., Open Cup	347°+	347°+	347°+	347°+	347°+	347°+	347°+
Softening-pt. ° F., Ring and Ball	95°–131°	95°–131°	104°–140°	104°–140°	104°–140°	113°–149°	113°–150°
Pen. 77° F., 100 g., 5 sec.*	120–150	100–120	85–100	60–70	50–60	40–50	30–80*
Ductility 77° F.	..	..	..	40+	40+	40+	40+
Loss 325° F., 5 hr., %	1·0–	1·0–	1·0–	1·0–	1·0–	1·0–	2·0–
Pen. resid., % original pen.	60·0+	60·0+	60·0+	60·0+	60·0+	60·0+	60·0+
Sol. in CS_2, %	99·5+	99·5+	99·5+	99·5+	99·5+	99·5+	99·5+
Org. insol. CS_2, %	0·2–	0·2–	0·2–	0·2–	0·2–	0·2–	..
Mineral matter, %	..	..	..	..	..	..	0·5–

* British Standard Specifications state: 'The Engineer shall specify a penetration figure for the asphaltic cement within the limits set out in the table and no material shall be used which varies more than plus or minus 5 points from the penetration figure so specified, that is the range of variation shall not exceed 10 points.'

When straight reduction of a given crude produces an asphalt cement of high susceptibility, this susceptibility may often be reduced by moderate oxidation or blowing near the end of the distillation process without markedly reducing the ductility of the asphalt. Moderate oxidation may therefore sometimes be advisable as a manufacturing process, although highly oxidized, low ductility products are usually eliminated in specifications for asphalt paving cements.

Table III shows the results of commonly used tests on asphalt cements produced from various sources, and Table IV gives typical specification requirements adopted by the United States and British Governments for asphalt paving cements.

It is seen that although there is considerable variation in characteristics of the individual asphalt cements in Table III, they all come within specification requirements of Table IV for the grade represented by 40 to 50 penetration limits. Prior to the more recent developments in refinery cracking operations under pressure, asphalt cements recovered from cracked residual base stock were eliminated by the usual solubility requirements in specifications. Under modern processes it is, however, quite possible to crack both reduced crudes and overhead, so that when the liquid cracked residual is further reduced to asphalt cement it can meet just as rigid solubility requirements as the straight-reduced cements. Such products are, however, viewed with suspicion by the highway engineer, as the earlier cracked asphalts proved to be unsatisfactory and the more recent ones have not as yet demonstrated their suitability for long-life high-type pavement construction.

Where it is desired definitely to eliminate all asphalts produced by cracking processes, reaction to the Oliensis Spot Test (cf. Analysis and Testing section) is included in specifications. Briefly described, this test consists in treating a small sample of the asphalt with a special type of naphtha in definite volume proportions and then placing a drop of the mixture on a filter-paper. The stain produced in the case of cracked asphalts consists of a well-defined spot or nucleus of black solid material, surrounded by a lighter uniform discoloration of the paper as shown in Fig. 2, A. In the case of straight-reduced asphalts, where temperature conditions during refining have not been severe, a uniform stain free from any nucleus or annular ring is produced as in Fig. 2, B. Between these two extremes variable types of stains may be noted, the significance of which is questionable, but which are probably related to the heat treatment to which the product has been subjected during manufacture. Thus a central spot or nucleus, free from solid material, but somewhat darker than the surrounding area, may be formed, and in some cases such a spot may be surrounded by a thin fringe or ring of solid material. Such stains do not identify a definite pressure-cracking process, but may indicate more severe temperature conditions during refining than in the case of a clean, uniform stain. The nucleus of black, solid material only should be considered as positive identification of asphalt produced by a definite cracking process. In such cases, asphalts formed by cracking overhead stock usually show a yellowish-brown stain surrounding the nucleus, while those produced by cracking reduced crudes show a light chocolate-brown stain in the outer area. While this test, which is described in further detail in the following paragraph, may be useful for the purpose above described as applied to asphalt prior to use, it should be noted that asphalts in general are sensitive to the action of sunlight and that thin films exposed to light for protracted periods undergo alterations in chemical and physical structure. Asphalt so exposed will sometimes react positively to the spot test, although the original product as delivered from the refinery may have reacted negatively.

Oliensis Spot Test. The naphtha solvent should be a straight-run overhead distillate free from cracked products of any kind, with an API. gravity of 49 to 50 and an aniline number of 138 to 145° F. Upon distillation the I.B.P. should be above 300° F. and E.P. below 410° F., with 50% over between 335 and 355° F. A weight of asphalt equivalent to 2 ml. is placed in a 25-ml. Erlenmeyer flask, and is cautiously heated in the flask on a hot plate till it flows out over the bottom. After cooling, 10·2 ml. of solvent are added; a stopper fitted with an 8-in. length of ¼-in. glass tubing is quickly inserted into the neck of the flask; the contents of the flask are swirled with a rapid circular motion for 5 seconds, and the flask is immediately immersed in a bath of gently boiling water (unless the sample is a thin liquid, in which case the heating bath is unnecessary). The contents of the flask is again swirled for 5 seconds and at the end of each minute thereafter until complete dispersion takes place. If dispersion is not completed in from 6 to 8 minutes, the test shall be repeated with the bath maintained at a 25° F. lower or higher temperature (glycerine being substituted for the water bath in the latter case) until dispersion is effected within the stipulated time. After complete dispersion, as judged by tilting the flask, the flask is allowed to cool to room temperature, and if any loss in weight occurs it is made up with additional solvent. A drop of the asphalt solvent mixture is then placed on the filter-paper. If the drop forms a brown or yellowish-brown circular stain, with a darker, solid, or annular nucleus in the centre, the test shall be reported as '*Positive*'.

Temperature Susceptibility. In general the temperature susceptibility of an asphalt cement within the range of ordinary atmospheric temperatures seems to be best indicated by the relation between its penetration and softening-point. Thus, for a given penetration, the higher the softening-point the lower the susceptibility. Holmes, Collins, and Childs have developed a general relationship between these two properties for straight-reduced asphalts from a large number of crude sources, expressed by the equation $M = kP^a$, where M is the Ball and Ring softening-point, P the penetration, and a and k constants, depending upon the source of the asphalt and the temperature at which penetration is measured. From data secured in their investigations they have constructed a chart (see Fig. 3) which is of considerable interest in numerically rating temperature susceptibility by means of a Softening-point Penetration Index. ('Measuring the Susceptibility of Asphalt to Temperature Changes', by A. Holmes, J. O. Collins, and W. C. Childs. Paper presented before the American Chemical Society, Petroleum Division, 22 April 1935.)

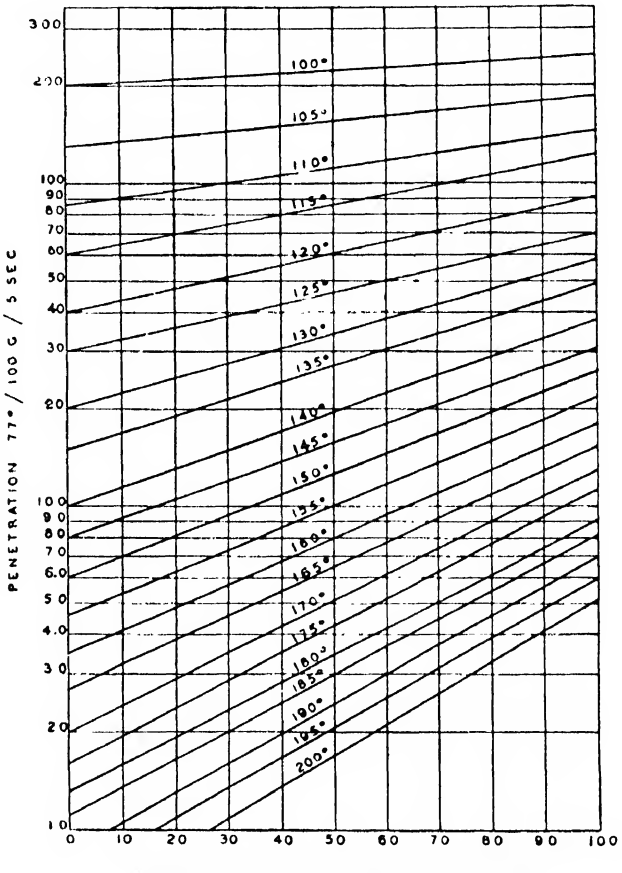


FIG. 3.

In this chart straight-reduced asphalts from heavy Mexican crude which have a relatively low susceptibility were arbitrarily established as 100 on the index scale, and asphalts produced as residues from the cracking of gas oil, which are highly susceptible to temperature changes, were chosen to represent the 0 on the index scale. It is claimed that straight-reduced asphalts from any given source will usually locate between typical indices for the source. The chart may therefore prove useful in roughly indicating the source of asphalts, or, if the source is known, it will indicate whether or not and to what extent the asphalt has been oxidized.

Thus, for example, the straight-reduced California asphalt in Table III, which has a penetration of 41 and a softening-point of 123° F., shows an index of approximately 20, while the oxidized California asphalt, with a

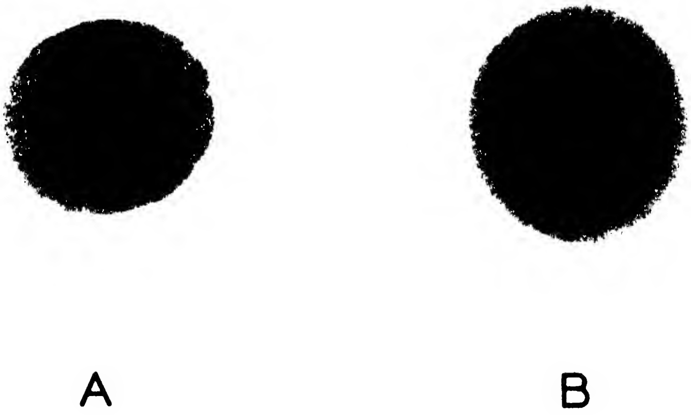


FIG. 2. Oliensis Spot Test

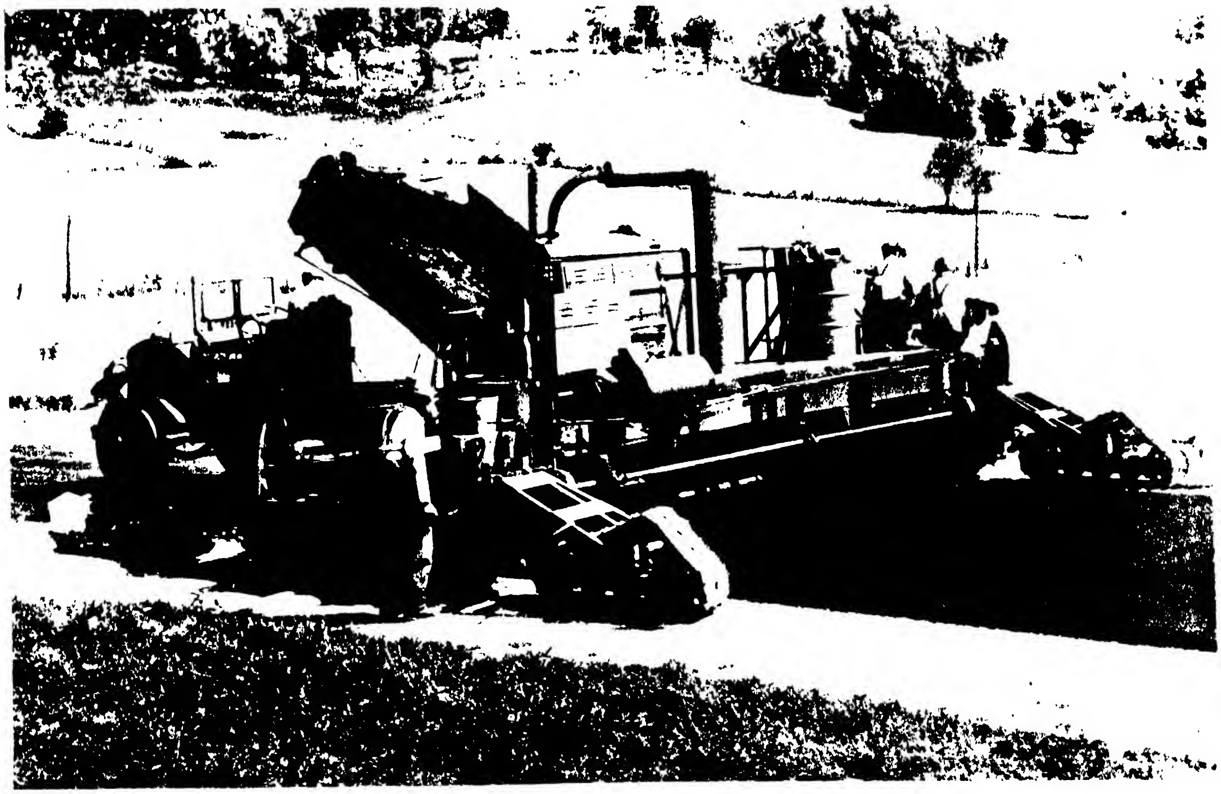


FIG. 5. Laying asphalt mixture with mechanical spreader

penetration of 41 and a softening-point of 135° F., shows an index of 85, being almost as high as the Mexican asphalt.

Hard Asphalts and Fluxes

In the early days of the asphalt paving industry it was quite common for contractors engaged in the manufacture of hot-laid paving mixtures to combine hard asphalt cements with flux so as to control the penetration of the product within any desired limits. With the old-type melting and heating equipment asphalt cements were often hardened to an undesirable extent by prolonged hot storage and had to be softened before use by the addition of flux oil. With modern improvements in equipment and operation there is now but little demand for flux to be used for this purpose.

As asphalt is a natural constituent of petroleum in which it is held in solution, it naturally follows that it will combine readily with most petroleum products. To produce a stable asphalt cement which will meet the usual specification requirements it is, however, necessary that the flux should have a high flash-point and show a low loss by volatilization. Residual oils of suitable viscosity are therefore ordinarily used as paving fluxes. The higher its viscosity the greater will be the amount of flux required to soften an asphalt of given penetration to any definite higher penetration. The proper proportions of any given asphalt and flux to produce an asphalt cement of given penetration should be determined by trial on small samples before large-scale operation is attempted.

Specifications for fluxes include the following requirements:

Paving Flux

Flash-pt. ° F., Open Cup	350° F.+
Penetration 77° F., 50 g., 1 sec.	350+
Loss 325° F., 5 hr., %	5−
Sol. in CCl_4, %	99·0+

Hard powdered asphalts are now used to some extent in the preparation of cold-laid paving mixtures. For the hard asphalt to be of any value as a cementing medium it is necessary that the mixture contain a suitable flux which, after the mixture has been laid, will amalgamate with the powdered asphalt to produce an asphalt cement of suitable consistency or penetration.

Hard asphalts are prepared at the refinery either in lump or powdered form. In the former case they are ground to a relatively fine state of subdivision before incorporation in the paving mixture. Hard native asphalts, such as refined Trinidad Lake and Cuban asphalt, are prepared in this manner in addition to petroleum asphalt. Most of the powdered petroleum asphalts are produced from cracked base stock or are blends containing cracked asphalt. With such products it is extremely important to use a carefully selected flux, as many fluxes which might be satisfactory for uncracked asphalts will not produce homogeneous asphalt cements when combined with cracked asphalts. As these relationships cannot at present be accurately covered in specifications for the individual constituents, it is advisable for the refiner who produces powdered asphalt to also manufacture a special flux for use with it. Such flux may be prepared from the cracked base stock from which the hard asphalt is derived.

In using powdered asphalt and flux to prepare a paving mixture, it is customary to first coat the mineral aggregate with flux and then incorporate the powdered asphalt. As amalgamation of asphalt and flux is not effected for some time after the mixture has been made, it is essential that the flux have a sufficiently high viscosity so that it will not drain off the mineral aggregate, but will remain uniformly distributed throughout the mixture. The proportions of asphalt and flux incorporated in the mixture are selected to produce, after complete amalgamation, an asphalt cement of any desired penetration.

Cut-back Asphalts

The term cut-back asphalt is commonly used to describe products consisting of asphalt cement fluxed or thinned with a volatile distillate. The function of the distillate is to temporarily liquefy the asphalt cement so as to facilitate its application and manipulation in highway treatment and construction. The distillate should be of such nature that after it has served this purpose it should separate from the mixture, leaving the asphalt cement in place as a bonding and waterproofing medium.

The hardening characteristics of cut-back asphalts or the rapidity with which they may be expected to revert to an asphalt cement, after application or use, depends upon the amount and character of the distillate which is present and upon conditions attending their use. The more volatile the distillate the more rapid will be the rate of hardening, other conditions being the same. However, the rate of hardening is also governed by the amount of distillate present, those containing a large amount of distillate hardening more slowly than those containing a smaller amount. Thus, when made from the same constituents, the more fluid products, under normal atmospheric conditions, require a longer time to revert to an asphalt cement than do the more viscous products.

The degree of fluidity of a cut-back asphalt is largely a function of the amount of distillate used in its preparation. Starting with a given asphalt cement, the more distillate present the more liquid becomes the final product. With a large amount of any light distillate an asphalt cement may be fluxed to almost water-thin consistency. With lesser amounts more viscous products are obtained of any desired consistency. In general, the harder the original asphalt cement, or the lower its penetration, the greater will be the quantity of a given distillate required to bring it to a given degree of fluidity. However, a marked difference is often found in the liquefying capacity of a given distillate for asphalts, of the same penetration obtained from different sources or produced by different processes, so that the amount of distillate present cannot be too intimately associated with the viscosity of the finished product. Failure to recognize this fact has, in some cases, been responsible for the development of specifications in which the relations between viscosity requirements, percentage of distillate recovered by test, and penetration of the recovered asphalt have been so close as to eliminate many products which would be entirely satisfactory for the intended use.

In general, asphalt cements of high-temperature susceptibility or low 'Softening-point Penetration Index' require less of a given distillate to reduce them to a given viscosity than do those of low-temperature susceptibility or high 'Softening-point Penetration Index'. Thus an asphalt cement of 60 penetration with an index of 0 may require but 22% of a given distillate to reduce it to a Furol viscosity at 122° F. of 200 sec., while an asphalt cement of the same penetration but with an index of 100 may require as much as 33% of the same distillate to reduce it to the same viscosity.

For the special uses to which cut-back asphalts are put in highway treatment and construction, products containing asphalt cements manufactured from cracked base stock have frequently given a good account of themselves, so that they are not looked upon with as much suspicion by the consumer as in the case of asphalt cements for the more durable hot-mix types of construction. Asphalt produced by cracking processes will not, however, produce stable cut-backs with all distillates which can be used for straight-reduced asphalts. It therefore becomes necessary for the producer to carefully select a suitable distillate in so far as its solvent value for such asphalts is concerned. Highly cracked distillates are best adapted for such products and, as a rule, also have a higher solvent value than uncracked distillates for the straight-reduced asphalts. Incompatible mixtures of asphalt cement and distillate, while apparently homogeneous immediately after manufacture, sludge out or sometimes jell upon standing in storage. No separation or jelling of any sort should occur during prolonged storage.

There are two general classes of cut-back asphalts used in highway work known as rapid curing and medium curing. The former are prepared with a naphtha-type distillate and the latter with a kerosine or light furnace-oil distillate. Both rapid- and medium-curing cut-backs are manufactured in a number of grades defined by viscosity limits, just as asphalt cements are graded by penetration limits. Their suitability for the various uses to which they are put is further evaluated by their ability to yield an asphalt cement within specified penetration limits when subjected to a standard distillation test which removes all or nearly all of their distillate constituent at a liquid-phase temperature of 680° F. Tables V and VI give typical specification requirements adopted by the United States Government and the Asphalt Institute for rapid-curing and medium-curing cut-back asphalts respectively.

TABLE V

Specifications for Type R.C. Asphaltic Road Materials

Specification designation	*R.C. 1*	*R.C. 2*	*R.C. 3*	*R.C. 4*
General requirement	The material shall be free from water and shall meet the following requirements when tested in accordance with the methods hereinafter enumerated.			
Flash-point (Open Tag.) ° F.	80+	80+	80+	80+
Furol viscosity at 122° F.	80–160	200–400	..	..
„ „ „ 140° F.	..	..	275–400	700–1,400
Distillation, % by volume:				
Total distillate to 374° F.	5+	..	..	..
„ „ „ 437° F.	12+	10+	3+	0·5+
„ „ „ 600° F.	25+	20+	14+	7+
„ „ „ 680° F.	40−	35−	30−	25−
Tests on residue from distillation:				
Penetration 77° F., 100 g., 5 sec.	60–120	60–120	60–120	60–120
Ductility at 77° F.	60+	60+	60+	60+
% soluble in carbon disulphide	99·5+	99·5+	99·5+	99·5+

TABLE VI

Specifications for Type M.C. Asphaltic Road Materials

Specification designation	*M.C. 1*	*M.C. 2*	*M.C. 3*	*M.C. 4*	*M.C. 5*
General requirement	The material shall be free from water and shall meet the following requirements when tested in accordance with the methods hereinafter enumerated.				
Flash-point (Open Tag.) ° F.	..	150+	150+	150+	150+
Furol viscosity at 77° F.	40–150	..	..	..	..
„ „ „ 140° F.	..	150–250	300–500	500–800	..
„ „ „ 180° F.	..	..	..	..	170–280
Distillation, % by volume:					
Total distillate to 437° F.	10−	2−	2−	1−	1−
„ „ „ 600° F.	25+	10–20	8–20	16−	14−
„ „ „ 680° F.	50−	27−	25−	25−	20−
Tests on residue from distillation:					
Penetration 77° F., 100 g., 5 sec.	70–300	100–300	100–300	100–300	100–300
Ductility at 77° F.	60+	60+	60+	60+	60+
% soluble in carbon disulphide	99·5+	99·5+	99·5+	99·5+	99·5+

It should be noted that all four grades of rapid-curing cut-back may be manufactured from a single asphalt cement and naphtha distillate by varying their proportions, and, in like manner, all five grades of medium-curing cut-back may be manufactured from the same asphalt cement and a light furnace-oil distillate. Three basic constituents from a single refinery may therefore produce all classes and grades of cut-back covered in these specifications.

Rapid-curing cut-back asphalts are used for the surface treatment of highways and for open-type aggregate wearing courses constructed by the road-mix or cold-laid plant-mix method. They are not suitable for use directly on dusty surfaces nor with mineral aggregates containing any appreciable amount of dust, as they tend to ball in such mixtures and do not readily distribute themselves uniformly throughout such aggregates. This is largely due to their very rapid increase in viscosity upon exposure to atmospheric conditions.

The R.C. 1 grade is best adapted for surface treatment as a seal coat or in the construction of thin, bituminous carpet courses with a light cover of suitable mineral aggregate free from dust. It is not intended for use as a primer on untreated roads, as it is apt to harden before it can penetrate the surface. Before application to non-bituminous surfaces the road should preferably be primed with Type M.C. 1 material.

The R.C. 2 grade provides for a rapid-curing liquid product of relatively low viscosity, suitable for the preparation of cold-patch mixtures, with open-graded mineral aggregate having little or no material passing the 10-mesh and practically none passing the 200-mesh sieve. If the asphaltic material is warmed prior to admixture with the mineral aggregate, suitable precautions should be taken to avoid fire hazard. The mixture should preferably be aged in stock piles for 24 hours or more before use. This material may also be used in cool weather for the type of construction described under R.C. 3.

The R.C. 3 grade provides for a rapid-curing product of relatively high viscosity suitable for use in the construction of roller-compacted road-mix wearing courses, or for cold-patch mixtures, in which the mineral aggregate is of the open type, consisting principally of crushed fragments, maximum size not over 1½ in., and practically all of which is retained on a ¼-in. screen. The asphaltic material should be warmed prior to application with suitable precautions to avoid fire hazard. It is not intended for use with aggregate containing a high dust content. Type R.C. 2 material may be used for this class of construction in cool weather, particularly in cases where the maximum diameter of mineral aggregate particle does not exceed 1 in.

The R.C. 4 grade provides for a rapid-curing product of high viscosity suitable for use in the construction of roller-compacted cold-laid plant-mix wearing courses in which the mineral aggregate is of the open type, consisting principally of crushed fragments, maximum size not over 1½ in. and practically all of which is retained on a ¼-in. screen. It is particularly adapted for use under conditions where the mixture is to be laid and compacted immediately after mixing. The asphaltic material should be warmed prior to use with suitable precautions to avoid fire hazard.

Medium-curing cut-backs are best suited for use with mineral aggregates of the dense-graded type. Unless of very high initial viscosity, it is desirable that the aggregate contain an appreciable amount of material finer than 200 mesh. They are used for a special kind of surface treatment, known as priming, and in the construction of close-mix wearing course by either the road-mix or cold-laid plant-mix method.

Specification M.C. 1 provides for a liquid product of very low viscosity for cold application, suitable for use as a primer for initial surface treatment of road surfaces preparatory to the construction of a bituminous carpet or wearing course. It is readily and completely absorbed by earth, gravel, or broken-stone surfaces, where it hardens in place. While it develops considerable cementitiousness upon drying, it is not intended to hold a cover of stone chips or gravel.

Specification M.C. 2 provides for a medium-curing liquid product of low viscosity suitable for use in the construction of traffic-compacted road-mix wearing courses in which the mineral aggregate is densely graded, from a maximum diameter of 1 in. down, with from 35 to 60% of material passing a 10-mesh sieve and from 7 to 14% passing a 200-mesh sieve. This material should ordinarily be warmed before application. Its viscosity increases materially after use so as to develop considerable cementitiousness. It is therefore adapted for the type of construction described, under severe climatic conditions. It does not, however, harden with sufficient rapidity to be used to best advantage as a binder for coarse, open, mineral aggregates free from dust.

Specification M.C. 3 provides for a medium-curing liquid product of medium viscosity suitable for use in the construction of traffic-compacted cold-laid plant-mix wearing courses in which the mineral aggregate is densely graded from a maximum of 1 in. down, with from 35 to 60% of material passing a 10-mesh sieve, and from 7 to 14% passing a 200-mesh sieve. It is also suitable for use in the construction of roller-compacted road-mix wearing courses in which the mineral aggregate is of the open-graded type with a maximum diameter of not over 1 in., containing little or no material passing the 200-mesh, but having a relatively high percentage passing the 10-mesh sieve. This material should be warmed before application. Its viscosity increases materially after use so as to develop considerable cementitiousness, and it is therefore adapted to both types of construction described, under severe climatic conditions.

Specification M.C. 4 provides for a medium-curing liquid product of relatively high viscosity suitable for use in the construction of roller-compacted cold-laid plant-mix wearing courses, or road-mix wearing courses in hot weather, in which the mineral aggregate is of the open-graded type with a maximum diameter of 1 in., containing little or no material passing the 200-mesh, but having not less than 35% passing the 10-mesh sieve. The asphaltic material and sometimes the aggregate require warming before mixing.

Specification M.C. 5 provides for a medium-curing product of high viscosity suitable for use in the construction of roller-compacted cold-laid plant-mix wearing courses, in which the mineral aggregate is of the open-graded type with a maximum diameter of 1 in., containing practically no material passing the 200-mesh, but having an appreciable percentage passing the ¼-in. screen. The asphaltic material and usually the aggregate require warming before mixing.

Liquid Residuals

Liquid residuals of the petroleum refinery, commonly termed 'road oils', include products of widely varying characteristics produced from a great variety of sources and in many different ways. Unfortunately there is no clear line of demarcation between road oils and residual fuel oils, as the former can always be used as fuel, and at the present time it is extremely difficult, if not impossible, to specify adequately a liquid residual in terms of commonly used tests so as to evaluate its usefulness for road purposes.

Asphalt cements can be specified to possess those properties which have been found to be desirable in a highly cementitious, water-resistant binder for highway structures. Cut-back asphalts are prepared from these asphalt cements with distillates which are known to separate from them and so leave a true asphalt in place in the road structure. They also can be specified with a considerable degree of assurance as to suitability for any given highway use. Liquid residuals, however, do not contain readily volatile distillates, and even if they carry a relatively high percentage of asphalt, their ability to develop this asphalt as a cementing material after application is difficult to evaluate because of the uncertain behaviour of the solvent oils which may be present.

Liquid residuals for highway uses were originally graded and specified according to their so-called asphalt content, or the percentage of asphalt cement of a designated penetration, usually 100 or 80, that they yield upon being subjected to a high-temperature evaporation test. Straight-reduced liquid residuals from California petroleum were first used for road purposes, and, as obtained from this source, it was found that their asphalt content was a rough measure of their viscosity. As residuals from other sources came on the market it was found that asphalt content was not a sufficiently accurate indication of viscosity, and at the present time it is customary to grade these products primarily by viscosity limits, although asphalt contents are also specified.

While the original viscosity of a road oil is of importance from the standpoint of its manipulation in highway treatment and construction, its value as a cementing medium is largely dependent upon the extent to which it approaches the consistency of an asphalt cement after application. Because of the non-volatile or only partially volatile character of the oily bodies in which the asphalt of the residual is held in solution, it is evident that this asphalt is never made available as a true asphalt cement through loss of volatile constituents after application. At the same time, with many residuals a marked increase in viscosity is possible through slow evaporation of a portion of such oily bodies. The more recent specifications, therefore, include a distillation test, such as used in evaluating cut-backs, together with a requirement for consistency of residue from distillation. During the past few years, however, investigations have shown that upon exposure in thin films to weather many road oils harden to a far greater extent than can be attributed to loss by volatilization. This is probably due to intramolecular reactions within the oily bodies which produce resinous or asphaltic constituents not originally present. No laboratory tests have yet been devised for determining the exact character of such changes or the extent to which they may be expected to occur.

Among the liquid residual asphaltic road materials which have been used with varying success, the following are listed to illustrate why, as a class, they exhibit such widely varying service characteristics:

1. Straight residuals run to desired viscosity.
2. Blends of straight residuals of different viscosities.
3. Very viscous straight residuals thinned to desired viscosity with light or heavy gas-oil distillates.

4. Residuals produced by cracking processes.
5. Blends of straight and cracked residuals.
6. Very viscous cracked residuals thinned with gas-oil distillates.

Of these some of the most satisfactory and also some of the worst behavers under service conditions are products manufactured by cracking processes, which in general seem to contain oily constituents most subject to rapid increase in consistency, not due to volatilization. The unsatisfactory materials of this type are those which lose all cementitiousness, either because of extreme hardening or the separation of constituent parts which were originally compatible mixtures or solutions. On the other hand, straight residuals which contain only very stable non-volatile oily constituents may not increase in viscosity or consistency after application to a sufficient extent to produce desired results. Depending upon the experience of individual consumers with products most readily available to them will be found those who wish to eliminate all cracked residuals by their specifications and those who have no desire to do so. When the Oliensis Spot Test, previously described, is specified for liquid residuals, the test is usually applied to the residue obtained from the distillation test.

Two general types of specifications are used for liquid residuals illustrated in Tables VII and VIII. The latter have been recommended by the United States Bureau of Public Roads and the Asphalt Institute.

TABLE VII

Specifications for Liquid Residual Road Materials

Specification designation	*30% oil*	*45% oil*	*60% oil*	*85% oil*
Specific gravity 77° F.	0·88+	0·90+	0·92+	0·95+
Furol viscosity, 77° F.	20–50	..	..	..
,, ,, 122° F.	..	20–50	150–300	..
,, ,, 210° F.	..	..	..	200–400
Loss 325° F., 50 g., 5 hr.	20–35	15–30	10–28*	10−
Residue 100 pen.	30–35	45–55	60–70	85+
Ductility residue 77° F.	60+	60+	60+	60+
Solubility in CS_2	99·5+	99·5+	99·5+	99·5+

* 60% oil is divided into two grades based on Loss at 325° F. Grade 1 loss 10–19 and Grade 2 loss 19–28.

TABLE VIII

Specifications for Type S.C. Asphaltic Road Materials

Specification designation	*S.C. 1*	*S.C. 2*	*S.C. 3*	*S.C. 4*
General requirement	The material shall meet the following requirements when tested in accordance with the methods hereinafter enumerated.			
Water and sediment, %	2−	2−	2−	2−
Flash-point (Cleveland Open Cup) ° F.	150+	200+	200+	250+
Furol viscosity at 77° F.	20–150	..	..	..
,, ,, ,, 122° F.	..	200–320	..	..
,, ,, ,, 140° F.	..	..	150–300	350–550
Distillation, % by volume:				
Total distillate to 437° F.	..	2−	2−	2−
,, ,, ,, 600° F.	..	15−	10−	8−
,, ,, ,, 680° F.	50−	25−	20−	18−
Tests on residue from distillation:				
Float at 122° F.	50−	25+	25+	25+
% soluble in carbon disulphide	99·0+	99·0+	99·0+	99·0+

Liquid residuals are used in the surface treatment and construction of low-cost roads. Their principal value for surface treatment is to lay dust. They are also used in the construction of road-mix and cold-laid plant-mix wearing courses with dense mineral aggregate, containing a substantial percentage of material finer than 200 mesh. In such construction they do not as a rule produce as durable results as the medium-curing cut-back asphalts.

In Table VIII specification S.C. 1 provides for a product of very low viscosity suitable for cold application as a dust layer. It may also be used for initial treatments in the progressive method of mat construction on soils or fine-grained aggregates where gradual improvement is to extend over a number of years with subsequent treatments employing more viscous asphaltic road materials. This product is not intended to serve as a hardening or cementing medium.

Specification S.C. 2 provides for a very slow-curing liquid product of low viscosity suitable for use in dry climates during cool weather in the construction of traffic-compacted road-mix wearing courses in which the mineral aggregate is densely graded, from a maximum diameter of 1 in. down, with from 35 to 60% of material passing a 10-mesh sieve and from 7 to 14% passing a 200-mesh sieve. It should ordinarily be warmed before application. This material may also be used in the blotter or mulch treatment of clay roads with a loose or floating cover of gravel aggregate.

Specification S.C. 3 provides for a very slow-curing liquid product of medium viscosity suitable for use in dry climates during hot weather, in the construction of traffic-compacted road-mix wearing courses in which the mineral aggregate is densely graded from a maximum diameter of 1 in. down, with from 35 to 60% of material passing a 10-mesh sieve and up to 14% passing a 200-mesh sieve. It requires warming before application.

Specification S.C. 4 provides for a very slow-curing liquid product of relatively high viscosity, suitable for use in dry climates in the construction of cold-laid traffic-compacted plant-mix wearing courses in which the mineral aggregate is densely graded from a maximum diameter of 1 in. down, with from 35 to 60% of material passing a 10-mesh sieve and from 7 to 14% passing a 200-mesh sieve. The asphaltic material and sometimes the aggregate require heating before mixing.

Hot-laid Asphalt Paving Mixtures

Hot-laid asphalt paving mixtures are used in the construction of the most durable high-type pavements and have a creditable service record covering a period of more than 50 years. The mineral aggregate is densely graded and bound together with asphalt cement which, for wearing courses, should be so proportioned that voids in the compressed mixture are reduced to a minimum. Asphalt cements used in their preparation are grades usually coming within the broad penetration limits of 40 to 70. The mineral aggregate usually consists of a mixture of two or more of the following products: commercial broken stone, broken slag, gravel, sand, and mineral filler such as pulverized limestone. The composition of the more common types of these mixtures, as defined by specification limits recommended by the Asphalt Institute, are shown in Table IX.

It will at once be noted that mineral aggregate constitutes the great bulk of all mixtures as the asphalt, represented by bitumen soluble in carbon disulphide, falls within the broad limits of only 4 to 12% by weight. As the specific gravity of mineral aggregates is slightly more than 2½ times that of asphalt, the actual volume proportion of asphalt in the compressed mixtures lies between the limits of 10 and 26%. Even from this standpoint it is evident that the skeleton structure of the mixture which carries the traffic load is mineral aggregate.

Hot-laid mixtures are prepared at an asphalt paving plant where the various aggregate constituents and the asphalt cement are stored, heated, proportioned, and

TABLE IX

Composition of Hot-laid Asphalt Paving Mixtures

Type	*Sheet asphalt*		*Asphaltic concrete*		
	Surface course	*Binder course*	*Stone-filled sheet asphalt*	*Surface course*	*Base course*
	%	%	%	%	%
Mineral aggregate	88–90·5	94–6	90·5–93	92–5	93–6
Pass 1½ in. retained ½ in. .	..	..	..	..	50–65
,, 1½ in. ,, ¾ in. .	..	..	..	..	20–30
,, 1¼ in. ,, ½ in. .	..	52–72	..	..	..
,, 1¼ in. ,, ¾ in. .	..	..	..	15–25	..
,, ¾ in. ,, ½ in. .	..	..	..	20–35	25–40
,, ⅝ in. ,, 10 mesh	..	..	20–35	..	..
,, ½ in. ,, 10 ,,	..	8–20	..	5–15	5–15
,, ½ in. ,, 200 ,,	..	15–35	..	..	..
,, 10 mesh ,, 200 ,,	..	..	..	25–35	10–35
,, 10 ,, ,, 40 ,,	10–40	..	7–30	..	..
,, 40 ,, ,, 80 ,,	20–45	..	11–40	..	..
,, 80 ,, ,, 200 ,,	12–32	..	10–30	..	..
,, 200 ,, (mineral filler)	10–20	..	7–12	4–6	..
Bitumen (soluble in CS_2) .	9·5–12	4–6	7–9·5	5–8	4–7

mixed. The principal parts of a hot-mix plant are shown in Fig. 4.

The aggregate drier usually consists of a long cylindrical rotating steel drum, mounted at a slight angle from the horizontal, and is internally fired. It not only heats the aggregate to the desired temperature, but removes all moisture. All aggregate constituents with the exception of mineral filler are run through the drier, after which they are passed over screens to separate them into suitable sizes for recombination, and each size is stored in a separate bin. The asphalt cement is brought to the desired temperature for mixing in kettles or tanks preferably heated by means of steam coils, and all piping should be steam jacketed. From the draw-off tank the hot asphalt is pumped or lifted by air-pressure through a steam-jacketed pipe to a draw-off cock for charging the asphalt weigh bucket, which is suspended on the mixing platform. Continuous circulation of the hot asphalt through the draw-off pipe with return to the draw-off tank is desirable. The mixing platform is located directly under the hot storage bins, and each mineral aggregate constituent is charged separately into a weigh box which holds the total charge for a batch. After the batch has been weighed it is dumped directly into the mixer, and after a short interval of dry mixing the asphalt is added and mixing continued until all particles are completely coated and distribution of asphalt throughout the mix is uniform. The most commonly used type of mixer is known as the twin-pug and consists of a rectangular steel box with semicylindrical bottom equipped with two shafts rotating in opposite directions, to which are attached mixing blades of such length and set at such angles as found most efficient. The mixer is set in the floor of the mixing platform at an elevation sufficient to permit discharge of the finished mixture through a full-opening bottom gate directly into trucks for transportation to the paving job.

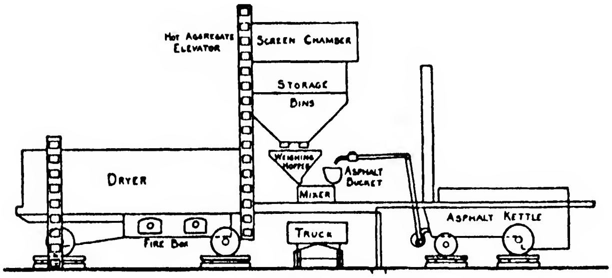


FIG. 4. Hot-mix plant.

Upon arrival of the hot mix on the job it is spread upon the prepared base in a uniform layer so as to produce, after compaction, the desired thickness. Shovels and rakes may be used for this purpose, although a mechanical spreader, such as shown in Fig. 5, is to be preferred. After spreading, the mixture is thoroughly compacted while still hot by means of heavy rollers. As soon as it is cooled the pavement may be opened to traffic. Asphaltic concrete wearing courses are usually laid to a finished thickness of 2 in. upon a suitable foundation. Sheet asphalt pavements are constructed in two courses each 1½ in. thick. The lower course, known as the binder, is laid directly upon the foundation and is covered with the sheet asphalt surface course. Asphaltic concrete foundations, or base course, are laid to a thickness of from 3 to 5 in.

The temperature at which the mixture is prepared and spread should be carefully controlled and never exceed 375° F. The lowest temperature compatible with proper workability during spreading and compaction is desirable. Excessive temperature is not only apt to harden and injure the asphalt films, but may result in drainage of a portion of the asphalt from the top to bottom of loads during transportation and so produce non-uniformity, resulting in an unsatisfactory pavement. A glance at Table III shows that asphalt cements from different sources may vary greatly in viscosity at 300° F. although of the same penetration at 77° F. It is quite evident, for instance, that a mixture made with the California asphalt of 74 viscosity will not require as high a temperature as one made with the Mexican asphalt of 191 viscosity in order that both may have the same degree of workability or plasticity.

Although the hot mixture as laid is very plastic, it hardens rapidly upon cooling. At its maximum service temperature, about 140° F. in temperate climates, the compressed mixture should be sufficiently stiff to resist displacement under the load and thrust of traffic, but a certain degree of plasticity is always desirable to prevent the development of cracks under temperature and loading stresses, which type of failure almost invariably appears in rigid monolithic pavements. Plasticity in the finished mixture is largely a function of the consistency and proportion of asphalt cement which it contains and is therefore controllable within certain limits. Resistance of asphalt paving mixtures to internal displacement or plastic flow is known as stability, and is measured by means of the stability test illustrated in Fig. 6. In this test a cylindrical briquette or core specimen of the compressed mixture is placed in a close-fitting cylinder, to the bottom of which is clamped

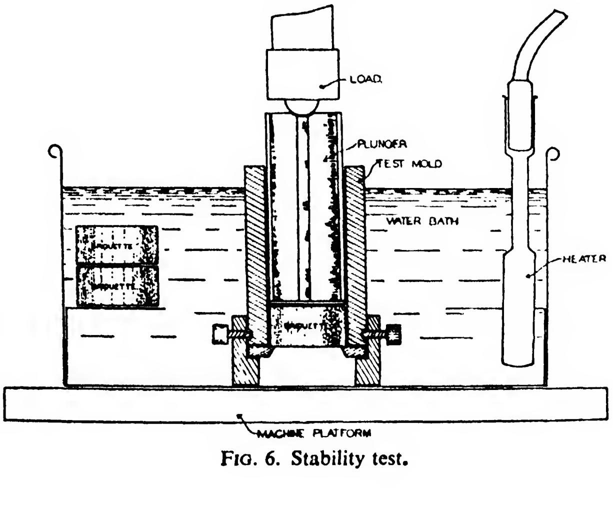


FIG. 6. Stability test.

a ring with a standard orifice. The temperature of the specimen is maintained at 140° F. or any desired temperature by immersion in a water bath. In making the test, load is applied under standardized conditions to the upper surface of the briquette by means of a close-fitting plunger, and the maximum load developed in forcing the mixture through the orifice is recorded as pounds stability.

Laboratory studies have shown that this test is not only useful in evaluating the mixture itself, but that it also serves as a means of determining the effect of variations in character and proportion of the individual constituents. To resist heavy traffic successfully it has been found desirable to use a mixture showing a stability value of not less than 2,000 lb. at 140° F.

All asphalt paving mixtures should be as waterproof as possible. High density or freedom from voids prevents water from entering the compressed mixture and causing trouble due to freezing and thawing. It also minimizes any tendency for water to displace the asphalt films, a trouble sometimes encountered in open-type or porous mixtures containing hydrophilic aggregates such as quartzite. Hot-laid wearing-course mixtures can and should be designed so that voids in the compressed mixture are not more than 5%. The presence of mineral filler which reduces the size of voids in the compressed aggregate to exceedingly small capillary diameters permits this to be accomplished without developing other objectionable characteristics when an asphalt paving cement is used as a binder. For reasons later discussed this cannot be done with liquid asphaltic products.

Voids in the compressed mixture may be calculated from the following formula in which V represents % of voids, D the maximum theoretical density, and d the actual determined density or specific gravity of the compressed mixture.

$$V = \frac{100(D-d)}{D}.$$

The value of D is determined by the formula

$$D = \frac{100}{W/G + W_1/G_1 + W_2/G_2,\ \&c.},$$

in which W, W_1, and W_2 represent the percentage weights of the individual constituents of the mixture, and G, G_1, and G_2 their respective specific gravities.

When designing the hot mix care must be exercised not to overfill the voids in the compressed mineral aggregate with asphalt, as otherwise the stability of the mixture will be greatly reduced and the surface will be soft and sticky in hot weather. As the coefficient of expansion for asphalt is greater than that for mineral aggregates, it is evident that if voids are completely filled at average service temperature they will be overfilled at maximum service temperature. A safety factor of 1½% minimum voids in the compressed mixture is ample provision against such trouble. In developing a suitable formula for the mix it is necessary to determine voids in the compressed mineral aggregate, exclusive of asphalt. This may be readily calculated from the data required for determination of voids in the compressed mixture, provided the mixture is not overfilled with asphalt. Thus the theoretical maximum density of the mineral aggregate D_1 would first be calculated from the following formula in which W, W_1, &c., represent the percentage weights of the mineral aggregate constituents and G, G_1, &c., their respective specific gravities.

$$D_1 = \frac{W + W_1,\ \&c.}{W/G + W/G_1,\ \&c.}$$

The apparent specific gravity of the compressed mineral aggregate d_1 as it exists in the mixture is calculated as follows:

$$d_1 = d(1 - \%\ \text{asphalt}).$$

Voids in the compressed mineral aggregate designated V.M.A. would then be determined as follows:

$$\text{V.M.A.} = \frac{100(D_1 - d_1)}{D_1}.$$

In a properly designed hot-laid paving mixture the film of asphalt surrounding each particle should be sufficiently thick that, when the mixture is compressed and the film thickness between points and areas of contact reduced to a minimum, the excess asphalt squeezed into the voids should almost, but not quite, fill them. The film will then be a continuous phase of variable thickness throughout the mixture. For any given type of graded mineral aggregate the average film thickness may be considered as a function of amount of asphalt in the mix. Other factors being constant, the thicker the average film the more resistant to water action and weathering becomes the mixture. Provided a satisfactory degree of stability is obtained, it therefore follows that the higher the percentage of asphalt the more durable will be the mixture. In other words, high void aggregates which can be almost filled with asphalt without undue sacrifice of stability should produce more durable mixtures than low void aggregates. This fact should be kept in mind, particularly in connexion with the design of mixtures to withstand severe moisture and temperature conditions.

From the preceding discussion it is evident that in the design of satisfactory hot-laid mixtures the factors of stability or plasticity, density or freedom from voids, and film thickness are of primary importance. When severe exposure to prolonged or constant water action is to be anticipated, selection of a hydrophobic aggregate such as limestone or one which has a preferential adsorption for asphalt over water is of importance. This is particularly true of mixtures of an open or porous structure, and will be further discussed in the following section.

A recent development in the use of a sheet asphalt type of mix for paving or revetting the banks of the Mississippi River to prevent further erosion at caving bends is of sufficient interest to warrant special mention in connexion with hot-laid mixtures. Briefly described, the process consists in constructing on the steel deck of a large barge sections of compressed paving mixture, reinforced with steel cables and wire mesh. By means of cables the first section is pulled on to the bank so that one edge is above the water line. While the other edge remains on the barge, a second section is constructed abutting the first and sealed to it with hot asphalt cement. This operation is repeated as the barge is pulled from under succeeding sections, allowing a continuous ribbon of the mixture, known as the asphalt mattress, to enter the water and come to rest on the slope of the under bank. When a sufficient length of the mattress has been constructed to reach the toe of the slope, the last section is lowered into position by means of the reinforcing cables which, with the mesh reinforcement, is continuous throughout the entire length of mattress. After one mattress has been placed, additional mattresses are laid parallel to each other with an overlap on the one previously constructed, until the bank of the river-bend has been protected. Fig. 7 illustrates the general scheme of operation.

Fig. 8. Asphalt mattress plant working off-shore in New Orleans Harbour

Fig. 9. Asphalt road mix construction

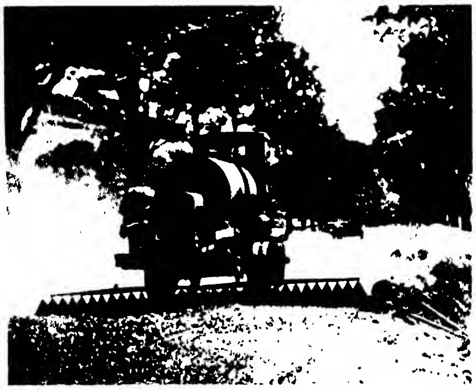


Fig. 10. Pressure distributor for applying asphalt

The asphalt revetment assemblage is shown working off shore in Fig. 8. An asphalt paving plant is located on a barge directly back of the enormous mattress barge, on the deck of which sections of mattress 217½ ft. by 30 ft. are constructed 2 in. thick with the metal reinforcing carried midway between the upper and lower surfaces. Each section of mattress weighs approximately 80 tons. The hot mixture is spread and compacted by means of two especially designed machines similar to those used in highway construction, and as soon as each section is compacted it is rapidly cooled by flooding the surface with water pumped from the river. When it has cooled to approximately 140°F. it is launched. The entire cycle of operation is approximately ½ hour. The total length of a single mattress 217½ ft. wide may at times exceed 600 ft., and in some locations it is placed in depths of water of over 160 ft.

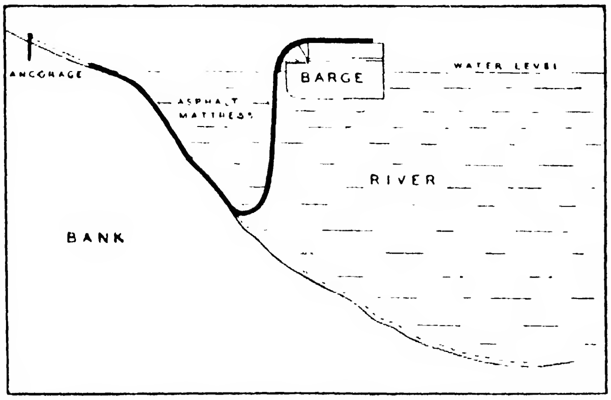


FIG. 7. Paving the bottom of a river with asphalt.

This work is being done by the United States War Department with which the Asphalt Institute co-operated in the design of the mixture. The formula selected for use after a careful study of available aggregates and stability, bend and water-action tests on mixtures, was as follows:

River sand passing 10 mesh	66%
Loess (about 90% passing 325 mesh)	22%
Asphalt cement 30–40 penetration	12%

Because flexibility rather than high stability was desired in this mixture, voids in the compressed mineral aggregate were slightly overfilled with asphalt. A relatively hard asphalt cement was used to impart desired tensile strength to the mixture at the temperature of launching.

Paving Mixtures containing Liquid Asphaltic Products

Paving mixtures prepared with liquid asphaltic products differ essentially from the hot-laid mixtures, as they cannot be designed to produce as great a degree of density and inherent waterproofness. They are apt to prove less durable under the most severe climatic and traffic conditions, although many have proved economical and satisfactory, particularly for use on secondary highways and on main highways where moderate traffic prevails. The character of mineral aggregate best suited for use with the various types and grades of liquid asphaltic products has been described in a previous section.

The mixtures may be prepared at a paving plant or directly on the road to be surfaced. In the former case the process of mixing is similar to that described for hot-laid mixtures except that a less elaborate plant is required. The aggregate seldom requires heating except to remove excess moisture. Mixtures prepared at a plant are spread and compacted while cold in a manner similar to hot mix, but an asphaltic seal coat is always desirable to waterproof the upper surface after compaction. Wearing courses are constructed on a prepared base to a finished thickness of from 1½ to 2½ in.

Road-mix construction is a comparatively simple operation and consists in first spreading the dry mineral aggregate over the entire road surface in a layer of uniform thickness. The liquid asphaltic material is then applied to the surface of the loose aggregate, at a predetermined quantity per unit area, by means of a pressure distributor. Aggregate and asphalt are then turned and mixed by means of harrows and road bladers or specially designed multiple-blade drags or road mixers, as shown in Fig. 9. As it is frequently impracticable to apply and mix all of the required asphaltic material at one time, a second and sometimes a third application and mixing operation may be required before the mixture is ready for compaction. Compaction of mixtures prepared with cut-back asphalts is usually effected with a road roller, but when liquid residuals are used traffic, accompanied by intermittent blading, may be depended upon for compaction.

Proportioning of liquid asphaltic material in the design of paving mixtures cannot be governed by the same rules applied to hot-laid wearing-course mixtures. In the latter, sufficient asphalt cement can be used to practically fill the voids in the compacted aggregate. This is practicable for two reasons: first, the void spaces are exceedingly small; and second, the asphalt cement has a sufficiently high viscosity at maximum service temperature to prevent its bleeding to the surface through the minute voids. If void spaces were relatively large, as would be the case with no mineral filler present in the mix, even the asphalt cement, in spite of its high viscosity, would creep or bleed to the surface in excess quantity.

There is therefore a very important relation between size of voids and viscosity of asphalt to be taken into account in the design of paving mixtures. Laws governing this relationship are not at present well understood, but experience has shown that with coarse open aggregates no asphaltic paving material can be proportioned so as to fill the voids without producing an unsatisfactory sticky surface. Moreover, it has been found that even with dense small-void aggregates containing mineral filler no liquid asphaltic material can be proportioned so as to fill the voids without producing a similar unsatisfactory surface condition. At the same time it should be borne in mind that use of the highest proportion of the asphaltic material that the aggregate can carry without surface bleeding or undue loss of stability is desirable from the standpoint of durability and resistance to water action. This can often be approximated by compressing trial mixtures differently proportioned and subjecting them to prolonged tamping at a temperature of 140° F. or slightly higher.

In all mixtures made with liquid asphaltic products the interfacial relation between aggregate and asphalt with relation to water is a matter of considerable importance, and the use of hydrophobic aggregates which have a preferential adsorption for asphalt and petroleum oils over water should be selected for use. Coarse aggregates such as used with the rapid-curing cut-backs can be tested for this property by first coating them with the cut-back so as to produce, after thorough aeration, a substantial film of asphalt cement and then agitating the coated fragments in water at a temperature of 140° F. If the asphalt film is readily stripped from the aggregate surfaces an undesirable hydrophilic aggregate is indicated. Riedel and Weber (*Asphalt-Teer-Strassenbautechn.* 31, 957 (1931)) recommend a more severe test to evaluate aggregates from this standpoint, which consists in mixing the aggregate, reduced to a given degree of fineness in definite proportions, with the binder and then boiling the mixture in water. If this test shows good adhesion of the film, additional samples of the mixture are boiled in solutions of sodium carbonate of increasing concentration, and the strength of solution required to remove the film is recorded as a measure of its adhesion tension.

As a water-action test for dense-graded aggregate mixtures containing an appreciable percentage passing the 200-mesh sieve, the following method, known as the swell test developed by the United States Bureau of Public Roads, may be used. One thousand grams of the mixture are placed in a cylinder 4 in. in diameter and 6 in. high and moulded under a pressure of about 2,000 lb. per sq. in. After compression the specimen is left in the mould and a slip cover, made of no. 40-mesh sieve supported in a frame, is placed flush against the underside of the mould. The mould containing the specimen is then placed in a water bath so that there is ⅛ in. of clearance from the bottom of the tank. The water-level in the bath is kept about 1 in. above the surface of the specimen, while the specimen in the mould is covered with about ½ in. of water. The amount of swelling is measured on the top of the specimen by means of an Ames dial, contact with the specimen being made by a thin metal disk 1 in. in diameter. Readings are taken at regular intervals until maximum swelling is obtained. A swelling of as little as 1/16 in. indicates that only mediocre success can be expected from the use of the particular aggregate. Aggregates entirely unsuitable for mixing have given swelling as great as ¾ in. under the conditions of this test.

Surface Treatment and Penetration

Asphalt surface treatments may be applied to almost every type of road or pavement. In the case of ordinary earth roads, where the primary purpose is to lay dust, a liquid residual of low viscosity such as specified in Table VIII under designation S.C. 1 may be used. When it is desired to produce a thin asphalt-bound mat on a sand-clay, gravel, or macadam road it is first desirable to prime the surface with a low viscosity medium-curing cut-back such as M.C. 1 material specified in Table VI, applied to the extent that it is completely absorbed by the road surface.

For a waterproof surface-mat construction or seal coat either a rapid-curing cut-back with relatively fine aggregate cover or a soft asphalt cement with relatively coarse aggregate cover may be used. Both should be applied uniformly over the surface by means of a pressure distributor such as illustrated in Fig. 10. In the case of a cut-back asphalt such as R.C. 1, specified in Table V, rate of application will usually be between 0·2 and 0·3 gal. per square yard with mineral cover of from 20 to 30 lb. per square yard, depending upon the amount of cut-back applied. Mineral aggregate may consist of sand for the lighter treatments, but preferably of rock or slag crushed and screened to pass a 1-in. or ¾-in. screen and be retained upon a ¼-in. screen. The aggregate should be practically free from dust and after application may be advantageously broom dragged until all particles are thoroughly coated and the films have dried sufficiently to bond under the roller.

When a soft asphalt cement is used for surface treatment, almost any grade softer than 150 penetration may be used. Before application such products should be heated until quite fluid and should be immediately covered after application. Depending upon the thickness of mat desired, the rate of application may be varied from 0·25 to 0·5 gal. per square yard with a cover of from 25 to 50 lb. of mineral aggregate thoroughly rolled as applied. It is not desirable to use sand or other fine aggregate for cover, as the mat is apt to bleed badly under traffic due to the excess of asphalt in immediate contact with the old road. Broken stone or slag passing a 1¼-in. screen and retained on a ½-in. screen is best used.

In the penetration type of construction, known as asphalt macadam, it is customary to lay a wearing course approximately 2½ in. thick. Typical specifications require that a layer of broken stone of from 2½ to 1¼ in. diameter be spread upon the prepared base in a uniform loose layer of suitable thickness and rolled until the fragments key together. Hot asphalt cement, commonly from 85 to 100 penetration, is then applied to the surface by means of a pressure distributor at a uniform rate of approximately 2 gal. per square yard. Immediately afterwards the surface voids are chinked with a light application of broken stone of from ¾ to ¼ in. diameter, thoroughly rolled. When the surface is firmly bonded all loose material is swept from the road and a seal coat of hot asphalt cement is applied at the rate of approximately 0·4 gal. per square yard and covered with the same size aggregate used for chinking the surface. Thorough rolling then completes the job. In the construction of the asphalt macadam no attempt is made to fill the voids in the coarse aggregate with asphalt for reasons described in the preceding section. By using the quantity specified, however, thick films of asphalt are produced and durable results assured, provided the aggregate is not highly hydrophilic. It is, of course, important that the aggregate be dry and free from dust when the hot asphalt is applied. To ensure good adhesion of the films this type of pavement should be constructed only in dry warm weather. In cold weather the asphalt cement chills so rapidly after application that it does not penetrate properly nor attach itself firmly to the aggregate surfaces.

A cut-back asphalt of high viscosity may sometimes be advantageously used for penetration construction in cold weather. For this purpose a product of somewhat higher viscosity than the maximum specified in Table V should be used.

Joint Fillers, Bedding Courses, and Asphalt Plank

For filling wide joints such as constructed in Portland cement concrete pavements an oxidized asphalt or a mineral-filled asphalt cement may be used. These products are heated to a fluid condition and poured into the joints so as to fill them to within ¼ in. of the top of the joint. This provides room for expansion of the asphalt in hot weather and prevents an excessive amount from being squeezed out and on to the surface of the pavement unless the joint becomes much narrower due to expansion of the concrete. Mineral-filled asphalts are usually manufactured by the petroleum refiner from an asphalt in which is suspended a certain percentage of mineral matter in a very fine state of subdivision. Slate dust is frequently used in such products. Typical specifications for the two types of fillers are as follows:

Oxidized Asphalt Filler

Specific gravity 77°/77° F.	1·00+
Flash-point, ° F., Open Cup	500°+
Softening-point ° F., Ring and Ball	167°+
Penetration 77° F., 100 g., 5 sec.	30–45
Penetration 32° F., 200 g., 60 sec.	15+
Penetration 115° F., 50 g., 5 sec.	90−
Ductility 77° F.	4+
Loss at 325° F., 50 g., 5 hr., %	1·0−
Soluble in CS_2, %	99·0+
Bitumen soluble in CCl_4, %	99·0+

Mineral-filled Asphalt

Penetration 77° F., 100 g., 5 sec.	80–100
Ductility 77° F.	30+
Loss 325° F., 50 g., 5 hr., %	2·0−
Inorganic insoluble in CS_2, %	15–26
Settling test, 2 hr., 325° F., inorganic insoluble in CS_2,	
Top sample, % deviation basis of mineral matter	15−
Bottom sample, % deviation basis of mineral matter	25−

Joint fillers consisting of premoulded strips of asphalt mixed with fine mineral substances, fibrous materials, cork, sawdust, &c., are patented products of variable composition. They are inserted in the joint slot and the surface usually sealed with a hot smoothing-iron.

For filling the rather wide joints between individual blocks in stone block pavements the mineral-filled asphalt is sometimes poured, but more often a hot grout, composed of approximately equal parts by volume of sand and an asphalt paving cement of 50–60 or 60–70 penetration, is flooded over the pavement surface and broomed into the joints.

Narrower joints, such as occur in brick pavements, are filled by flooding the surface with hot oxidized asphalt and working it into the joints with hot iron squeegees. A more recent method which is finding considerable favour consists in first spraying the newly laid brick surface with a separating agent, either whitewash or a mixture of calcium chloride, laundry starch, and water. The oxidized asphalt filler is then heated to a temperature of 400 to 450° F. and flooded over the surface so as to fill completely the joints. The surplus filler, when nearly cold, is removed in strips from the upper face of the bricks by cutting with a spading tool. The portion removed may be remelted and used again.

Narrow cracks which form in various pavements are often filled with a rapid-curing cut-back asphalt such as specified under designation R.C. 1 in Table V. A light sanding adjacent to the crack takes up all surplus which may occur on the surface.

Bedding courses for brick and block pavements are made with a mixture of dry sand and liquid asphalt material such as that specified under designation M.C. 2 in Table VI or S.C. 2 in Table VIII. The mixture usually contains from 5 to 8% by volume of the asphaltic material, the exact quantity being governed by the behaviour of the mixture, which should be of such consistency as to strike off smoothly and compact under the templet, but not displace under the bricks or blocks as they are laid. Sometimes stone blocks are set in a hot-mix mastic bedding course quite similar in composition to sheet asphalt.

Asphalt planks are largely used for paving bridge floors. They are somewhat similar in composition to the preformed joint fillers, but are stronger and less compressible. Their average composition will usually come within the following limits:

Asphalt cement, %	35–50
Organic fibre, %	13–18
Mineral filler, %	40–50

They are made in 3- and 6-ft. lengths and in 6- and 8-in. widths, of varying thickness running from ¾ to 2 in. Some have a plain upper surface and some are surfaced with mineral particles of from ¼ to ¾ in. diameter, embedded into the plank matrix under pressure. They are made in straight side and ship-lap cross-sections.

Asphalt plank may be nailed to a wooden deck or cemented with hot asphalt cement to a concrete deck.

TYPICAL ASPHALT SPECIFICATIONS FOR ROAD AND PAVEMENT CONSTRUCTION

By **J. S. MILLER, Jr., A.I.C.E.**

Chemical Engineer, Barber Asphalt Company

In order to acquaint the reader with the type of specification usually drawn for asphalts to be used in road and pavement construction, the specifications issued by the governments of the United States of America, Germany, Great Britain, and France are reproduced below. It should be noted that the American and British specifications attempt to differentiate between asphalt from various sources. This emphasizes the manner of overcoming difficulties one encounters in attempting to draft an all-inclusive specification, which by its very liberal breadth of purpose must exclude tests for desirable properties.

UNITED STATES OF AMERICA FEDERAL SPECIFICATION FOR ASPHALT

FOR USE IN ROAD AND PAVEMENT CONSTRUCTION

A. *Applicable Federal Specifications.*

A. 1. There are no other Federal specifications applicable to this specification.

A. 2. Any special requirements of the individual departments are noted under section H.

B. *Types and Grades.*

B. 1. This specification covers the types and grades of materials shown in Table I. The material shall be supplied in the particular type (or types) and grade (or grades) ordered.

TABLE I

Grade (penetration)	*Type of material*	*Designation*
120–150	Petroleum asphalt	AP. 1–25
120–150	Fluxed native asphalt	AB. 1–25
100–120	Petroleum asphalt	AP. 2–25
100–120	Fluxed native asphalt	AB. 2–25
85–100	Petroleum asphalt	AP. 3–25
85–100	Fluxed native asphalt	AB. 3–25
60–70	Petroleum asphalt	AP. 5–25
60–70	Fluxed native asphalt	AB. 5–25
50–60	Petroleum asphalt	AP. 6–25
50–60	Fluxed native asphalt	AB. 6–25
50–60	Fluxed native asphalt	AT. 6–25
40–50	Petroleum asphalt	AP. 7–25
40–50	Fluxed native asphalt	AB. 7–25
40–50	Fluxed native asphalt	AT. 7–25

C. *Material and Workmanship.*

C. 1. The materials supplied under this specification shall be asphalts prepared by the distillation of asphaltic petroleum or by the fluxing of hard native asphalts with a suitable petroleum flux.

C. 2. Those materials only which have been demonstrated by service tests as satisfactory for the intended use will be acceptable under this specification.

C. 3. No mineral matter other than that naturally contained in the asphalt shall be present.

D. *General Requirements.*

D. 1. The asphalt shall be homogeneous, free from water, and shall not foam when heated to 175° C. (347° F.).

E. *Detail Requirements.*

E. 1. Physical and chemical properties. The respective types and grades shall meet the requirements shown in Table II.

TABLE II

Physical and Chemical Properties

Designation	*AP. 1–25*	*AB. 1–25*
(1) Specific gravity 25°/25° C. (77°/77° F.)	Not less than 1·000	1·025–1·050
(2) Flash-point, not less than	175° C. (347° F.)	175° C. (347° F.)
(3) Softening-point	35–55° C. (95–131° F.)	35–45° C. (95–113° F.)
(4) Penetration at 25° C. (77° F.), 100 g., 5 sec.	120–150	120–150
(5) Ductility at 25° C. (77° F.), cm., not less than	..	..
(6) Loss at 163° C. (325° F.), 5 hr., not more than	1·0%	3·0%
(*a*) Penetration of residue at 25° C. (77° F.), 100 g., 5 sec., as compared to penetration before heating, not less than	60·0%	50·0%
(7) Bitumen (soluble in carbon disulphide), not less than	99·5%	95·0%
(*a*) Organic matter insoluble, not more than	0·2%	..
(*b*) Inorganic matter insoluble, not more than	..	1·5–2·5%

Designation	*AP. 2–25*	*AB. 2–25*
(1) Specific gravity 25°/25° C. (77°/77° F.)	Not less than 1·000	1·040–1·060
(2) Flash-point, not less than	175° C. (347° F.)	175° C. (347° F.)
(3) Softening-point	35–55° C. (95–131° F.)	40–50° C. (104–22° F.)
(4) Penetration at 25° C. (77° F.), 100 g., 5 sec.	100–120	100–120
(5) Ductility at 25° C. (77° F.), cm., not less than	..	..
(6) Loss at 163° C. (325° F.), 5 hr., not more than	1·0%	3·0%
(*a*) Penetration of residue at 25° C. (77° F.), 100 g., 5 sec., as compared to penetration before heating, not less than	60·0%	50·0%
(7) Bitumen (soluble in carbon disulphide), not less than	99·5%	95·0%
(*a*) Organic matter insoluble, not more than	0·2%	..
(*b*) Inorganic matter insoluble, not more than	..	1·5–3·0%

Designation	*AP. 3–25*	*AB. 3–25*
(1) Specific gravity 25°/25° C. (77°/77° F.)	Not less than 1·000	1·050–1·070
(2) Flash-point, not less than	175° C. (347° F.)	175° C. (347° F.)
(3) Softening-point	40–60° C. (104–40° F.)	40–50° C. (104–22° F.)
(4) Penetration at 25° C. (77° F.), 100 g., 5 sec.	85–100	85–100
(5) Ductility at 25° C. (77° F.), cm., not less than	..	..
(6) Loss at 163° C. (325° F.), 5 hr., not more than	1·0%	3·0%
(*a*) Penetration of residue at 25° C. (77° F.), 100 g., 5 sec., as compared to penetration before heating, not less than	60·0%	50·0%
(7) Bitumen (soluble in carbon disulphide), not less than	99·5%	95·0%
(*a*) Organic matter insoluble, not more than	0·2%	..
(*b*) Inorganic matter insoluble, not more than	..	1·5–3·0%

TABLE II (*cont.*)

Designation	*AP. 5–25*	*AB. 5–25*
(1) Specific gravity 25°/25° C. (77°/77° F.)	Not less than 1·010	1·050–1·070
(2) Flash-point, not less than	175° C. (347° F.)	175° C. (347° F.)
(3) Softening-point	40–60° C. (104–40° F.)	45–55° C. (113–31° F.)
(4) Penetration at 25° C. (77° F.), 100 g., 5 sec.	60–70	60–70
(5) Ductility at 25° C. (77° F.), cm., not less than	40	40
(6) Loss at 163° C. (325° F.), 5 hr., not more than	1·0%	3·0%
(*a*) Penetration of residue at 25° C. (77° F.), 100 g., 5 sec., as compared to penetration before heating, not less than	60·0%	50·0%
(7) Bitumen (soluble in carbon disulphide), not less than	99·5%	94·5%
(*a*) Organic matter insoluble, not more than	0·2%	..
(*b*) Inorganic matter insoluble, not more than	..	2·0–3·5%

Designation	*AP. 6–25*	*AB. 6–25*	*AT. 6–25*
(1) Specific gravity 25°/25° C. (77°/77° F.)	Not less than 1·010	1·050–1·070	1·200–1·250
(2) Flash-point, not less than	175° C. (347° F.)	175° C. (347° F.)	175° C. (347° F.)
(3) Softening-point	40–60° C. (104–40° F.)	45–55° C. (113–31° F.)	45–55° C. (113–31° F.)
(4) Penetration at 25° C. (77° F.), 100 g., 5 sec.	50–60	50–60	50–60
(5) Ductility at 25° C. (77° F.), cm., not less than	40	40	40
(6) Loss at 163° C. (325° F.), 5 hr., not more than	1·0%	3·0%	3·0%
(*a*) Penetration of residue at 25° C. (77° F.), 100 g., 5 sec., as compared to penetration before heating, not less than	60·0%	50·0%	50·0%
(7) Bitumen (soluble in carbon disulphide), not less than	99·5%	94·0%	68·0%
(*a*) Organic matter insoluble, not more than	0·2%	..	..
(*b*) Inorganic matter insoluble, not more than	..	2·5–4·0%	20–30%

Designation	*AP. 7–25*	*AB. 7–25*	*AT. 7–25*
(1) Specific gravity 25°/25° C. (77°/77° F.)	Not less than 1·010	1·055–1·075	1·210–1·270
(2) Flash-point, not less than	175° C. (347° F.)	175° C. (347° F.)	175° C. (347° F.)
(3) Softening-point	45–64° C. (113–49° F.)	45–55° C. (113–31° F.)	50–60° C. (122–40° F.)
(4) Penetration at 25° C. (77° F.), 100 g., 5 sec.	40–50	40–50	40–50
(5) Ductility at 25° C. (77° F.), cm., not less than	40	40	40
(6) Loss at 163° C. (325° F.), 5 hr., not more than	1·0%	3·0%	3·0%
(*a*) Penetration of residue at 25° C. (77° F.), 100 g., 5 sec., as compared to penetration before heating, not less than	60·0%	50·0%	50·0%
(7) Bitumen (soluble in carbon disulphide), not less than	99·5%	94·0%	65·0%
(*a*) Organic matter insoluble, not more than	0·2%	..	..
(*b*) Inorganic matter insoluble, not more than	..	2·5–4·0%	22–32%

E. 2. Uniformity. The material furnished under this specification for a given contract, type, and grade shall be uniform in character and shall not vary more than 10° C. in softening-point from the test limits specified in Table II, nor more than 0·02 in specific gravity where no maximum limit is specified.

F. *Methods of Testing.*

Tests of the physical and chemical properties of the asphalt shall be made in accordance with the following methods:

F. 1. Specific gravity—A.S.T.M. Standard Method D. 70–27.

F. 2. Flash-point—A.S.T.M. Standard Method D. 92–24.

F. 3. Softening-point—A.S.T.M. Standard Method D. 36–26.

F. 4. Penetration—A.S.T.M. Standard Method D. 5–25.

F. 5. Ductility—A.S.T.M. Tentative Standard Method D. 113–26 T.

F. 6. Loss on heating—A.S.T.M. Standard Method D. 6–30.

F. 7. Bitumen (soluble in carbon disulphide)—A.S.T.M. Standard Method D. 4–27.

G. *Packing and Marking.*

G. 1. Any special requirements of the individual department are noted under section H.

H. *Requirements applicable to Individual Departments.*

H. 1. The following departmental specifications of the issue in effect on date of invitation for bids shall respectively form a part of this specification.

H. 1*a*. Army: U.S. Army Specification No. 100–2. Standard Specification for Marking Shipments.

H. 1*b*. Navy: Navy Department General Specifications for Inspection of Material, copies of which may be obtained without cost upon application to the Bureau of Supplies and Accounts, Navy Department, Washington, D.C.

I. *Notes.*

I. 1. It is the purpose of this specification to describe asphalts suitable for ordinary types of bituminous construction by physical and chemical requirements without prejudice as to source.

I. 2. The bidder shall state in his bid whether he proposes to furnish asphalt of a petroleum type, a fluxed native type, or both, and he shall also state the source or sources from which the material is derived.

I. 3. Bids shall be solicited on all types of asphalt of particular grade (or grades) desired.

I. 4. In connexion with this specification, see Federal Specification R-T. 121, Refined Tar for Construction, which covers an alternate material suitable for use in the construction of bituminous macadam roads.

I. 5. The materials covered by this specification are intended for use in the construction of bituminous roads and pavements, as shown in Table III.

TABLE III

Designation	*Intended use*
AP. 1–25 AB. 1–25	Bituminous macadam, northern United States, comparatively light traffic.
AP. 2–25 AB. 2–25	Bituminous macadam, middle United States or northern United States, comparatively heavy traffic.
AP. 3–25 AB. 3–25	Bituminous macadam, southern United States.
AP. 5–25 AB. 5–25	Graded bituminous concrete, northern United States, light or moderate traffic.
AP. 6–25 AB. 6–25 AT. 6–25	Graded bituminous concrete, southern United States or northern United States, heavy traffic. Sheet asphalt, northern United States, light or moderate traffic.
AP. 7–25 AB. 7–25 AT. 7–25	Sheet asphalt, southern United States or northern United States, heavy traffic.

I. 6. The information shown in Table III is necessarily general in character and should not be interpreted too strictly. Varying combinations of climate, traffic, and nature of the non-bituminous portion of the road or pavement will often influence the selection of the bituminous material and its method of use.

I. 7. The right is reserved to make award for that type (or types) of asphalt, and from that source (or sources) which in the judgement of the purchaser is best suited for his particular requirements.

I. 8. It is believed that this specification adequately describes the characteristics necessary to secure the desired material, and that normally no samples will be necessary prior to award to determine compliance with this specification. If, for any particular purpose, samples with bids are necessary, they should be specifically asked for in the invitation for bids, and the particular purpose to be served by the bid sample should be definitely stated, the specification to apply in all other respects.

I. 9. This specification governs all United States Government purchases of this commodity. Users are requested to retain this specification in permanent file until a revision is issued.

I. 10. Interested parties are advised that an Alphabetical Index of Federal Specifications may be obtained upon application as noted in the next paragraph, price to be obtained from Superintendent of Documents.

I. 11. Copies of this specification may be obtained upon application, accompanied by money order or coupon, or cash, to Superintendent of Documents, Government Printing Office, Washington, D.C. Price 5 cents.

I. 12. The penetration limits set forth in Table I do not conflict with the Recommendation for Simplified Practice, Bureau of Standards, Department of Commerce, Washington, D.C.

Notice.—When Government drawings, specifications, or other data are used for any purpose other than in connexion with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded, by implication or otherwise, as in any manner licensing the holder or any other person or corporation or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

BRITISH STANDARD SPECIFICATION FOR ROLLED ASPHALT

FLUXED NATURAL ASPHALT AND ASPHALTIC BITUMEN

Hot Process

B.S.I. 595—1935

Natural Asphalt and Asphaltic Cement

6. (*a*) *Natural Asphalt.*—This shall consist of material as defined under Clause 2 (*d*), and in addition shall, as mined, also comply with the following requirements:

Specific gravity	1·48–1·60
Soluble in CS_2	36–52%
Disseminated mineral matter	40–65%

(*b*) *Asphaltic Cement.*—The asphaltic cement as selected for binder and/or wearing surface shall comply with the appropriate specification given in the following table.

The engineer shall specify a penetration figure for the asphaltic cement within the limits set out in the table and no material shall be used which varies more than plus or minus 5 points from the penetration figure so specified, that is, the range of variation shall not exceed 10 points.

The exact proportions of natural asphalt and flux shall be determined by adequate laboratory tests, and shall be varied in accordance with the type of flux employed and the penetration of the asphaltic cement desired.

Properties of Asphaltic Cement

Property	*Asphaltic cement*					
	1		*2*		*3*	
	Asphaltic bitumen		*Fluxed natural asphalt*		*Equal proportions of asphaltic bitumen of appropriate penetration and natural asphalt*	
	Min.	Max.	Min.	Max.	Min.	Max.
Specific gravity at 60° F. (15·5° C.)	1·00	1·06	1·18	1·60	1·24	1·40
Flash-point (open), ° F. (° C.)	347 (175)	..	347 (175)	..	347 (175)	..
Softening-point (Ring and Ball), ° F. (° C.)	113 (45)	150 (65)	113 (45)	176 (80)	113 (45)	176 (80)
Penetration at 77° F. (25° C.)	30	80	30	80	30	80
Ductility at 77° F. (25° C.), cm.	40	..	10	..	40	..
Solubility in carbon disulphide (%)	99·5	..	43	70	65	76
Mineral matter (%)	..	0·5	26	60	20	35
Loss on heating for 5 hr. at 325° F. (163° C.) (%)	..	2·0	..	2·0	..	2·0
Penetration of residue after heating (percentage of original penetration)	60	..	60	..	60	..

Notes. (i) The above tests shall be performed in conformity with the methods set out in the current edition of *Standard Methods of Testing Petroleum and Its Products* published by the Institution of Petroleum Technologists.

(ii) If the engineer desires to use an asphaltic cement composed of an asphaltic bitumen and natural asphalt in other than equal proportions, as specified above, he shall specify such proportions when inviting tenders. Such alternative asphaltic cement shall be taken to comply with the requirements of this Specification if its flash-point, softening-point, penetration, loss on heating, and penetration after heating comply with the requirements set out for asphaltic cement No. 3 above, and its specific gravity, solubility in CS_2, and content of mineral matter comply with values calculated proportionately, according to the proportions of the mixture, based upon the figures of asphaltic cements Nos. 1 and 2 above, and of the specification of the particular natural asphalt used within the limits laid down in Clause 6 (*a*).

BRITISH STANDARD SPECIFICATION FOR ROLLED ASPHALT

FLUXED LAKE ASPHALT AND ASPHALTIC BITUMEN

Hot Process

B.S.S. 594—1935

(Superseding B.S.S. Nos. 342, 343, 344, 345,—1928)

Asphaltic Cement

6. The asphaltic cement as selected for binder and/or wearing surface shall comply with the appropriate specification given in the following table.

The engineer shall specify a penetration figure for the asphaltic cement within the limits set out in the table and no material shall be used which varies more than plus or minus 5 points from the penetration figure so specified, that is, the range of variation shall not exceed 10 points.

Properties of Asphaltic Cement

Property	*Asphaltic cement*					
	1 *Asphaltic bitumen*		*2* *Refined lake asphalt (fluxed)*		*3* *Equal proportions of asphaltic bitumen of appropriate penetration and refined lake asphalt*	
	Min.	Max.	Min.	Max.	Min.	Max.
Specific gravity at 60° F. (15·5° C.) . . .	1·00	1·06	1·20	1·34	1·17	1·20
Flash-point (open), ° F. (° C.)	347 (175)	. .	347 (175)	. .	347 (175)	. .
Softening-point (Ring and Ball), ° F. (° C.)	113 (45)	150 (65)	113 (45)	150 (65)	113 (45)	150 (65)
Penetration at 77° F. (25° C.) . . .	30	80	30	80	30	80
Ductility at 77° F. (25° C.), cm. . .	40	. .	25	. .	40	. .
Solubility in carbon disulphide (%) . .	99·5	. .	60	70	75	79
Mineral matter (ash) (%)	. .	0·5	26	32	17	19
Loss on heating for 5 hr. at 325° F. (163° C.) (%)	. .	2·0	. .	2·0	. .	2·0
Penetration of residue after heating (percentage of original penetration)	60	. .	60	. .	60	. .

Notes. (i) The above tests shall be performed in conformity with the methods set out in the current edition of *Standard Methods of Testing Petroleum and its Products* published by the Institution of Petroleum Technologists.

(ii) If the engineer desires to use an asphaltic cement composed of an asphaltic bitumen and refined lake asphalt in other than equal proportions, as specified above, he shall specify such proportions when inviting tenders. The properties of such alternative asphaltic cement shall be determined in the following manner:

The foregoing table is based upon asphaltic bitumen (ash-free) and refined lake asphalt (ash 36%). Varying proportions of asphaltic bitumen and refined lake asphalt will therefore be represented by a proportional ash content and such asphaltic cement shall be taken to comply with the requirements of this Specification if its flash-point, softening-point, penetration, loss on heating, and penetration after heating comply with the requirements set out for asphaltic cement No. 3 above, and its specific gravity, solubility in carbon disulphide, and content of mineral matter comply with values calculated proportionately, according to the proportions of the mixture.

FRANCE

Model Form of Tender Applicable to the Supply of Pure Bitumen Submitted by the Minister of Public Works to Chief Engineers

The following example is taken from Le Gavrian (*Les Chaussées modernes*, 2nd ed., Paris, 1935).

'Art. 2. *Quality of the Product.* The asphaltic bitumen which is the object of the present purchase shall be defined by the following characteristics:

(*a*) Essential characteristics:

Melting-point (Ring and Ball method).
Penetration at 25° C., 100 g., 5 sec. (standard apparatus A.S.T.M.).
Ductility (Dow method).
Solubility in CS_2.

(*b*) Useful characteristics:

Specific gravity at 25° C.
Flash-point (Cleveland apparatus).
Solubility in CCl_4.
Paraffin content (Richardson method).

'*Note on the subject of the Characteristics of Asphaltic Bitumen*

'The present state of knowledge of the relations between the Specifications for asphaltic bitumen and the service of the product on the road, under the varying circumstances of its use, do not yet permit of definitely fixing the essential physical and chemical characteristics of the bitumen. Nor does it permit the determination, with absolute precision, of the limits within which it is desirable to vary these characteristics.

'Nevertheless, if one refers to the conclusions of the International Committee created by virtue of the resolutions of the International Road Congress of Milan, as well as to the results of experience, it can be admitted, until further notice, that the essential characteristics are:

1. Penetration at 25° C., 100 g., 5 sec. (standard apparatus A.S.T.M.).
2. Melting-point (Ring and Ball method).
3. Ductility (Dow method).
4. Solubility in CS_2.

the useful characteristics being:

1. Specific gravity at 25° C.
2. Flash-point (Cleveland apparatus).
3. Solubility in CCl_4.
4. Paraffin content (Richardson method).

without pretending, in the present state of knowledge, that this enumeration is limitative.

'Now, without awaiting the result of the studies which will be undertaken soon, it is of the greatest importance to employ, in the various Services which utilize asphaltic bitumen, a form of tender in which the bitumen is the object of Specifications comprised within limits, of uniform definition, outside of which the material supplied will not be accepted, fixing for the present and provisionally, for these limits, fairly wide figures.

'With this idea, the figures to be inserted in Article 2 of the tender form should be in accordance with the following, for the four classes of bitumen which can be distinguished at the present time:

Property	*Class A*	*Class B*	*Class C*	*Class D*
Melting-point (Ring and Ball)	36–48° C.	42–54° C.	48–65° C.	60–120° C.
Ductility at 25° C. (Dow method) . . .	Over 100*	Over 100	Over 80	. .
Penetration at 25° C. .	140–220	80–140	40–80	Under 40
Specific gravity at 25° C.	1–1·04	1·01–1·05	1·02–1·06	Over 1·03

* Minimum susceptible of being increased when laboratories are equipped with apparatus permitting the measurement of ductility above 100.

Solubility in CS_2 . . .	over 99·5%
Flash-point, Cleveland method .	over 230° C.
Solubility in CCl_4 . . .	over 99%
Paraffin content	under 3%

'The characteristics indicated above do not apply to asphaltic bitumens naturally containing mineral matter (Trinidad bitumen, for example).'

GERMANY

GERMAN STANDARDS COMMITTEE SPECIFICATIONS

(DIN. 1,995 revised 1934)

A. *Specifications for Quality of Bitumen*

	Class				
	Bit. I	*Bit. II*	*Bit. III*	*Bit. IV*	*Bit. V*
1. Specific gravity at 25° C.	1·0	1·0	1·0	1·0	1·0
2. Drop-point (Ubbelohde)	Shall be at least 18° C. higher than the softening-point (K-S)				
3. Softening-point (R. and B.), ° C.	27–37	38–44	45–49	50–54	55–58
„ (K-S), ° C.	16–24	25–30	31–35	36–40	41–45
4. Break-point (Fraass), ° C.	−20	−15	−10	−8	−6
5. Penetration at 25° C.	..	210–150	150–80	80–50	50–30
6. Ductility at 25° C., at least	..	100	100	100	50
7. Ash, maximum	0·5%	0·5%	0·5%	0·5%	0·5%
8. Solubility in CS_2 or chloroform (min.)	99·0%	99·0%	99·0%	99·0%	99·0%
9. Paraffin, max.	2·0%	2·0%	2·0%	2·0%	2·0%
10. Weight loss after 5 hr., 163° C., max.	2·5%	2·0%	2·0%	2·0%	2·0%
11. Increase in softening-point (K-S) after heating, ° C., max.	10	10	10	10	10
12. Break-point after heating, min., ° C.	−15	−10	−8	−6	−5
13. Decrease in penetration at 25° C. after heating, max.	..	60	60	60	60
14. Decrease in ductility at 25° C. after heating, max.	..	60	60	60	60

When using Trinidad asphalt as an addition to road tar, a minimum content of 56 weight % of bitumen soluble in carbon disulphide or chloroform is required. The content of mineral matter (ash) must not exceed 37 weight %.

The German specifications include methods of test which have not been accepted generally outside Germany.

BITUMINOUS PAINTS

By L. A. JORDAN, D.Sc., F.I.C., A.R.C.S., M.I.Chem.E.

CONTENTS

I. GENERAL

Bitumen has been a familiar substance to mankind throughout the ages, but the extent to which bituminous substances are utilized in the arts to-day, and the consequent great commercial importance of these materials, is even more remarkable than the manner in which their supply has been continuously augmented during recent years, notably from petroleum residues. Although the context of this article suggests that particular regard should be paid to the use in 'paint' of the asphaltic bitumens particularly derived from petroleum residues, and this point has been borne in mind, it has been found necessary to treat the subject on a fairly wide basis; indeed, it would be wholly misleading to attempt to restrict reference to one class of bituminous substance only, for to a greater or lesser extent they are all material for the same type of paint. In detail it is true that different bitumens produce paints of different properties and different performance values, but such differences are more of degree than of function.

The description 'bitumen' or 'bituminous substance' can be limited or it can cover a wide range of substances, but we are concerned here to include all those materials of a certain general character which the paint manufacturer might use as bituminous materials. The list ranges from the asphaltic materials, substantially soluble in carbon bisulphide, which may be mined or obtained from asphaltic base petroleum, to the pitches obtained from fatty acids, rosin, and like materials. It is admitted that a more exact definition of the word 'bitumen' would exclude the fatty acid pitches.

In this article the words 'paint' and 'bituminous paint product' will be used at times in a general sense, meaning a protective coating material. Frequent reference must necessarily be made to 'bituminous varnish', 'japan', and 'bituminous paint', the word 'paint' being used then in a particular and narrow sense; these terms clearly indicate special forms and treatments of the base material capable of being applied to a surface by brushing, spraying, or dipping, but in order to save repetition of these special terms, they will collectively be spoken of as 'bituminous paint products'. The term 'bituminous paint' is usually applied, and will be here applied, to that type of product which consists substantially of bituminous base with volatile solvents with or without added pigment. It should be noted that in paint technology the word 'paint' signifies a pigmented product, but this rule does not apply to bituminous products which if pigmented are often referred to as 'pigmented bituminous compositions'. It is also difficult to indicate the boundary line between bituminous paints and other bituminous products. In general, the proportion of volatile solvent added to the bituminous base determines the consistency of the material and whether it is applied by brush or by trowel, that is, whether it is a paint or a cement; again, bituminous products similar in consistency may be applied, as by a trowelling machine to some textile material or paper and be regarded as paint, or to brickwork, as a damp-resisting coating, and called cement. Nothing is to be gained by attempting to define the field of interest more closely, but it is well to know how widely divergent can be the uses of such bituminous products.

The method of use of bituminous substances, wholly or in part as medium for 'paint', forms an established and highly specialized branch of paint technology with its own devotees, and, though scanty, its own literature. The high appreciation of bituminous substances as paint material is mainly due to their unique properties of resistance to acids, alkalis, and atmospheric influences generally, with low permeability to water and easy applicability in painting form. Naturally, different types show these properties to a widely varying extent, but the reaction to such tests can be extremely good. The principal handicap against even wider use of bituminous material than is the case to-day is the black colour, but that deficiency can be mitigated to some extent in emulsion paints and by the careful selection of the bitumen for use with suitable pigments. Some progress has been made with the production of light coloured bitumens (by removing the asphaltenes) which have a much reducing staining power, permitting pigments to cover the brown-black shade more easily.

of vapour into the air. Efficient ventilation is necessary, and only when such is provided should these chlorinated solvents be used as components of bituminous or other paints for use in enclosed spaces·

The determining factors in the selection of a solvent are intrinsic solvent action, flash-point, and evaporation rate.

(i) **Solvent Action.** Obviously the greater the *intrinsic solvent action* the less will be the amount required to produce a paint of desired consistency, and such determinations are a matter of experiment with the bituminous substance under test.

The solubility question will be complicated by the use of mixed bituminous materials and by the presence of non-bituminous material such as rosin in the mix. Vegetable oils and fats and fatty acid pitches usually increase the solubility of the bituminous base if the whole mix is properly fluxed. Indeed, these materials may almost be regarded as plasticizers for the harder bitumens. Of the pitches the fatty acid and rosin pitches are much more easily dissolved than tar products, some of which, notably coal-tar pitch, are largely insoluble in light petroleum naphtha. The native asphalts have a wide general solubility in the solvents mentioned which makes their handling easy; the petroleum bitumens, and particularly the air-blown grades, are also freely soluble and much more satisfactory in work than some of the pitches and similar residual products.

To some extent the choice of solvent will be affected by considerations other than solubility, for example, the proportion of solvent to base, which in commercial products may vary considerably with the intended purpose. Heavy material will probably carry high boiling solvent, whilst light bodied material, with which it is desired to secure great penetration, rapid drying, &c., will probably contain 50% or more of comparatively light boiling solvents. Furthermore, experience shows that the softer the bitumen the lighter should be the solvent.

One of the complications due to the use of solvent mixtures or other components than bitumen arises from the possibility of some part of the solvent mixture having selective and limited solvent action only on some part of the base, resulting in cloudiness and non-homogeneity in the film; as a general rule a non-homogeneous film lacks mechanical strength, so that this aspect of the matter is important even if exceptional. The good appearance of the dried film is also dependent upon the solvent characteristics in another sense. The gloss of a film is largely governed by the smoothing out which takes place in a film surface soon after the primary set, and the solvent then remaining must depart sufficiently slowly to allow time for irregularities of the surface to disappear. It is important that all bituminous media should be made and the solvent added at as low a temperature as possible consistent with achieving a proper distribution of the components. Detailed reasons will be given for this statement later, but mixing at too high a temperature may promote a separation, or at least disturb the state of dispersion, of the free carbon in the mix with disastrous effects on the film appearance.

(ii) **Inflammability** is often the determining factor in the selection of solvent in material which must be transported. The railway companies classify inflammable liquids:

(1) Those flashing below 73° F. (closed test)
(2) „ „ between 73° F. and 150° F.,

and both are described as dangerous.

The flash-point is the temperature at which the minimum explosive concentration of inflammable vapour and air is reached in the approved apparatus. The flash-point of a mixture of inflammable liquids is not necessarily that of the lowest flashing constituent or even the mean.

(iii) **Evaporation Rate** is another important aspect of solvent property generally regarded as determining the drying time of the painted-out film, but the rate of evaporation of solvent from a drying film is more than a mere matter of time. Some control is necessary of the rate at which the volatile liquid leaves the film, in order to regulate the flow of the material, to prevent the deposition of water from the atmosphere, and in the case of non-homogeneous products, to prevent premature separation of one component from the mix. All these matters affect the condition of the film. In the past, endeavours have been made to evaluate the evaporation characteristics of solvents under ordinary conditions by consideration of boiling-points, but this is unsatisfactory; although high boiling-points are, in general, associated with comparatively low evaporation rate and vice versa, the connexion between the two characteristics is inconstant and far from reliable. Furthermore, the addition of one solvent to another may profoundly modify the resultant rate of evaporation, while the presence of solid matter such as bitumen may have considerable and varied effects on the relative rates of evaporation of the liquids present. It is evident, therefore, that evaporation rates of liquids used in bituminous paint products can only be measured in a direct manner by a determination of the actual quantity of each particular liquid (single and in admixture) lost in a definite time from a definite surface area of the paint material evaporating in free air (or under other defined conditions) at known temperature and humidity. Temperature increase has the effect of accelerating the evaporation rate of all ordinary solvents, but there is reason to believe that humidity effects are important. If the solvent is miscible with water, high humidity retards the evaporation rate through deposition of atmospheric water on the film surface. If the solvent is immiscible with water, as in most of the material likely to be used in this work, the effect of humidity is less completely understood, for there is some evidence to show that very high humidity may accelerate the rate of evaporation, probably as a result of low atmospheric pressure.

(iv) **Viscosity.** The subject of *viscosity*, or to use a better word when compositions containing solid matter are considered, *consistency*, that is, the condition which determines the workability of the paint, must be considered as part of the solvent problem. The greater the proportion of solvent used the lower the consistency, but all solvents do not lower the consistency of bitumen to the same extent, e.g. straight petroleum bitumens require less solvent to reduce to equal consistency than native material such as gilsonite, or in other words, the viscosity/composition as well as the viscosity/temperature graphs fall more rapidly in the one case than in the other. The above aspects, however, would of themselves present no difficulty in control of production. The problems arise because of variations in consistency of different batches of what purports to be the same material, and particularly the fact that the consistency condition of a bituminous paint quite frequently changes with time, thickening up taking place to such an extent that the material may become in the limit quite unworkable. This condition of structural viscosity is akin to the 'livering' or 'fattening' of ordinary paint and varnish materials; it is particularly apt to occur with certain fatty acid pitches and with gilsonite, though the defect is usually less apparent when coal-tar naphtha is used owing to the high solvency of this material. It has been suggested [1, 1932] that a tendency to show structural viscosity is a function of the asphaltene content of bitumen, but the observation probably means that the asphaltene content is most susceptible to degradation and oxidation by heat.

Pigmentation of the bituminous paint also has a bearing upon the gelation problem, though in a rather different and special form.

(v) **Flow Properties of Bituminous Paints.** The simplest form of bituminous paint is a solution of a bituminous material in a solvent without the addition of drying oil, pigment, &c. Solutions in the hydronaphthalenes flow extremely well and give good films, usually of high gloss and free from brush marks and irregularities; these remarks apply to both air-dried and stoving finishes. Solutions in toluol or solvent naphtha may not remain open under the brush for a sufficient time, and hence exhibit bad brush marking; the addition of 20% or so of tetra- or decahydronaphthalene to bituminous solutions in toluol materially enhances their flow properties. Bituminous paints containing drying oils, &c., usually yield tougher and more resistant films than the straight bitumen solutions; in this case, too, the flow properties may be improved by the addition of the hydronaphthalenes, although the addition of the oil itself tends to assist the flow.

(*b*) Oils and Resins as Components

Some oil and resin are usually found in bituminous paint products, and such additions give a quality to the 'feel' or 'body' of the material under the paint brush, a quality which is missing in compositions consisting of bitumen in solvent only. This 'body' is particularly important in pigmented systems, for without it pigments are not easily held in suspension.

The oils used are mainly linseed and tung oil, either alone or more often mixed, but from time to time special products may contain other oils such as rape-seed and fish oils. The oils must, of course, dry by oxidation, and metallic siccatives are necessary to stimulate the drying process, though such materials have no drying effect on the bitumen component of the mix.

Linseed oil is, of course, the most commonly used material, and when properly incorporated with the bitumen (and in the main only the harder types of bitumen are used for this class of product) extremely desirable films can be produced, which, when compared with straight bituminous films, show improved adhesion, flexibility, gloss, and general durability performance. The oil may be used raw or thickened by heat treatment to produce a 'stand' oil, and indeed the method of manufacture of the bituminous product is closely concerned with the type and quality of oil used. The unique property of tung oil, namely, its capacity for rapid gelation under heat, imposes a special technique for the use of this material, to which reference will be made later.

When resins form part of the mix, as much consideration has to be given to the nature of the oil/resin as to the bitumen/resin complex. Most of the natural resins commonly met with in varnish-making practice could be used in making bituminous products, but price considerations rule out most of them and the special qualities of others would be lost; thus the principal natural resins used in bituminous products are rosin, both straight and in the lime-hardened form, and to a limited extent copal gum.

Coumarone is another resin very frequently found as a component of bituminous paints, particularly in combination with tung oil. Tung oil/coumarone varnishes have an acknowledged resistance to hydrolysis, particularly under alkaline conditions, and they make a desirable addition to a bituminous mix. Then there is to-day a large and rapidly increasing use of synthetic resins, particularly the modified phenolic type, as components of bituminous paints, and the results obtained with these products fully justify their inclusion.

The proportion of oils to bituminous matter may vary greatly. A typical formula might contain bitumen, resin, heat-thickened oil, and thinner, in the proportions 4 : 1 : 1 : 4, but many bituminous varnishes contain as much or even more oil than bitumen; they are also commonly made 'short oil', that is, a ratio of about 1 part of oil to 4 or 5 parts of bitumen, but even this proportion of oil is sufficient to modify profoundly the appearance, toughness, performance value, and general physical properties of the films. They have higher gloss, increased elasticity, flexibility, and toughness. The fatty acid pitch which is frequently a component of bituminous varnishes and japans also confers great flexibility on the film, and is used for this specific reason.

Mention has already been made that the oil component must dry by oxidation, but the drying quality of this class of composite material is not the arithmetic sum of the drying quality of the components, that is, the bitumen drying by loss of solvent and the oil drying by oxidation. Indeed, it is not unusual to have to make allowance for what appears to be an inhibition effect of the bitumen on the drying of the oil. The trouble is most marked in products of low bitumen content because there is not sufficient bitumen present to mask the effect by its own setting capacity. Probably the petroleum bitumens are most troublesome in this respect, and native material of the gilsonite type the least, but even so, the drying time of oils is increased enormously in the presence of quite small amounts of gilsonite. When the bitumen exceeds the oil component of the mix in amount, the drying weakness is not noticed so much, not because it does not exist, but because it is covered up by the hardness of the bitumen as such. Whether in any particular case these effects are due to some specific impurity in the bitumen, capable of acting as an anti-oxidant and so poisoning the oil-drying process, or to the presence of sulphur compounds, or of mineral oil not removed from a petroleum bitumen, or to adsorption of the metallic drier in the oil by the highly dispersed free carbon often present in the bitumen, or to the distribution of the oil as discrete particles of emulsion instead of in true solution, it is difficult to say, but probably all these factors operate. These problems are not yet satisfactorily solved. The obvious step is to provide sufficient drier to satisfy the adsorption and still leave sufficient to dry the oil; it is also desirable to secure that the drier is thoroughly incorporated with the oil before it meets the bituminous component, and this practice is usually followed. Fortunately the excess of drier necessary in bituminous oil products seems to have no deleterious effect on the life of the film, suggesting that when the drier is removed by adsorption from the oily phase it is no longer dispersed, not even in the bituminous adsorbent, and is in consequence innocuous. The extent of the heat treatment of the bitumen and oil also affects the drier problem, and whilst everything which has been said so far about the heat treatment is in favour of low temperature and the minimum of heating, nevertheless, it must be admitted that what would be regarded in the ordinary way as excessive heating from the point of view of the bitumen does, as a rule, improve the drying of the oil component considerably.

(*c*) Pigments

Consideration of coloured bituminous paints requires a sense of proportion. Manufacturers desire to produce material of attractive appearance with all the good properties of a bituminous film. Oil/resinous compositions carrying from 5 to 10% of selected bitumen can obviously be pigmented to almost any shade, as the staining quality of such a low concentration of bitumen is necessarily slight, but it may be doubted whether such paints are truly described as bituminous paints. In the ordinary way, 5% addition does not seem very much, but the effect of 5% of bitumen on the properties of an oil or oil/resin product is so marked as to produce in effect a different material. The vital change so made in the characteristics of a paint justifies the term 'bituminous' being applied to such materials. On the other hand, a paint with a substantial if not actually dominant bitumen content can only be produced in certain shades, mostly reds, deep yellows to browns, olive-green, drab stone colours, and deep greys according to the pigments used.

The pigments commonly used include red iron oxide, red lead, chromium oxide, lead chromate, yellow ochre, lithopone, zinc oxide, white lead, titanium oxide, graphite, carbon black, &c., and metallic powders and pastes. The choice of pigment must be made as carefully as the choice of bitumen, for all pigments intended to be used in bituminous products should possess high tinting strength and should be incorporated in a finely divided state. For the most part, mineral pigments are most satisfactory in bituminous paints, for they combine good staining quality and stability with relative cheapness.

Colour stability is particularly important, because very often the pigment is incorporated into the mix by simple stirring of the hot tanked material, and any colour sensitive to heat would be useless. The better class of bituminous paints, however, are ground either in the ready mixed form or, better still, in paste form, following the usual paint-making practice.

Graphite as a pigment is used with bituminous mixes to confer a higher degree of heat resistance on the product, whilst the metal pigments are, of course, in a class by themselves as far as preventing deterioration of the film of bitumen is concerned.

The selection of the bitumen for use in coloured products would depend very much upon the colour desired, and a test is conveniently made by judging the colour of a painted-out solution of the bitumen on a glass plate. The most severely decolorized bitumen will be brown in thin film, and in consequence it is difficult to produce light colours which are really clean.

The settlement of pigment from straight bituminous solutions is another serious problem, for more of the diluent or solvent of the bitumen is required if the bitumen is thickened up with pigment than without. That is why the simplest type of bituminous paint is seldom pigmented, or at least only lightly. It would almost be correct to say that no coloured bituminous product is made except on a bitumen/oil or oil varnish base, and even then trouble may be experienced with settlement of pigment. Some considerable success has been obtained with the prevention of settlement by the addition of filler materials such as asbestine or bentonite, which is a colloidal clay. The aluminium salts of the fatty acids are also useful for this duty. Heavy pigments naturally tend to settle rather more quickly than the light ones, but the density of the individual pigment is one of the least important considerations in determining the chances of settlement in the paint.

Pigmented products gain by reason of the fact that the films are harder and show increased resistance to abrasion and to flowing. The flowing of the more simple types of bituminous films long after they are dry in the ordinary sense has always been a serious defect, and it is worthy of note that films produced from emulsions of equivalent material are less prone to this defect; the reasons for this will be considered later. Pigmented bituminous materials and those containing substantial proportions of varnish medium do not offend in this way, whatever the manner in which the films are produced, because the pigment confers rigidity on the film.

Perhaps one of the most interesting developments in connexion with pigmented bituminous paints is the preparation of bitumen aluminium combinations. In this type of product polished aluminium powder, either dry or in paste form is mixed with straight bituminous paint, for example, gilsonite or petroleum bitumen in benzene or some other solvent which promotes the leafing effect of the aluminium powder. On the evaporation of the solvent the aluminium forms a 'skin' on the surface of the bituminous mass of the film, giving a product with all the protective qualities of bitumen combined with the bright finish of the aluminium. After storage of the paint for some time the aluminium tends to lose its leafing quality, probably due to the solution of the polishing agent from the surface, so that if the material is not to be used at once, the aluminium should not be added until just before use. The leafing quality seems to be definitely connected with the condition of the metal, including the shape of the particles, the type of vehicle, and the polishing agent, usually stearic acid.

(*d*) Bitumens

An indication has been given above of the extent and variety of different paint products which are being produced commercially from bituminous material. In turn, the manufacturer has to make the choice of the specific raw material to be used from the extensive range of bituminous substances available. The simplest type of bituminous paint referred to above may be made from the choicest grades of mineral gilsonite, or from petroleum asphaltic bitumens, or from coal-tar pitch. The gilsonite product will have good appearance and give hard films of considerable elasticity, possessing a coefficient of expansion very close to that of iron, so that the painting of iron may be undertaken with confidence and rust prevention is facilitated. Very much the same kind of report, differing only in degree, could be given about the product if petroleum bitumen had been used in its formulation, and coal-tar pitch is not unlikely to give a satisfactory protective coating, especially if applied to ironwork warm, although the finish may not be so attractive as the others mentioned.

Probably the most common defect of films prepared from these simple solutions is webbing or wrinkling; conditions due to shrinkage forces developing in the body of the film after initial surface skinning by rapid loss of solvent. Mitigation of this defect can usually be secured by making the loss of solvent more uniform throughout the thickness of the film, that is, by the use of rather less volatile materials. This subject connects with what has already been said about evaporation rates of solvents.

In practice, of course, the comparatively expensive native asphalts are found to be unnecessary for general purpose material of the simple type quoted in the above example, that is, the extra quality of performance does not as a rule justify the extra cost. Other examples may be given in which the bitumen, forming only part of a complicated mix, must be selected with due regard to its compatibility with the other components. In making bituminous/oil compositions the harder grades of bitumen are required, whilst it is generally accepted that gilsonite ranks first as the base for coloured bituminous paint products.

To make a right selection in any particular case requires experience backed by adequate knowledge of the properties of the material. Consequently, and running parallel with the large post-war development in this field of work, there has been a growing demand for more and more precise information about the properties of bituminous materials, tests, and methods of analysis, both on the original bitumen and on the products made therefrom. This demand is quite reasonable, although difficult to satisfy because bituminous materials, generally, whether they are native or manufactured, are by no means constant in their properties or compositions, in spite of every effort on the part of the bitumen technologist to make them so. The properties are controllable during manufacture, but they are not static in the sense that the composition and properties of an oil such as linseed oil can be taken for granted. For paint purposes it is usually not necessary to proceed to ultimate analysis or to carry out more than a small number of the many tests devised for the examination of bitumen for one purpose or another at different times. In any case, a chemical analysis as such avails nothing without some intimate knowledge of the physical properties of bituminous materials to assist the judgement. The tests such as are usually carried out by a paint technologist on the original bituminous material or on material separated from a bituminous paint preparation are really *Tests of Identification and Quality* or *Tests to indicate Suitability for a Given Purpose*. They may be listed as:

(i) **Colour, Streak, and Lustre of Fractured Surface.** The 'streak' test is very valuable as an indication of the suitability of the material for use in coloured products. Observations of colour in dilute solution and in thin film support the streak test. The lustre of a freshly fractured surface is also useful, the bright hard types of bitumen being most suitable for the manufacture of bituminous/oil compositions. The lustre test is best applied to material melted and allowed to stand. A lustreless or dull surface indicates the presence of mineral matter or too much free carbon (non-mineral matter insoluble in carbon bisulphide) or the 'sweating' out of something from the matrix in a blended product, and suggests that the material is unsuitable for use in bituminous paint products. Any lack of homogeneity may also be conveniently observed in thin film by the use of the microscope at a magnification of about 100.

(ii) **Behaviour on Heating, Softening-point, and Volatile Matter.** The odour and general behaviour on heating, and particularly the amount of volatile matter lost in an oven heated at from 325° F. to 500° F., are of great importance in identification and general factory control, particularly for those uses in which it is necessary to heat the bituminous substance considerably. The softening-point, however, is the most commonly used all-round test.

(iii) **Solubility in Carbon Bisulphide** and in petroleum naphtha and non-mineral matter insoluble in carbon bisulphide (free carbon). The solubility in carbon bisulphide is often the basis of purchase; as a rule the larger the percentage of matter soluble in carbon bisulphide, the greater the value of the material; for that reason the test is an important one. A high 'free-carbon' content is often, but not necessarily, proof that the material has been overheated, and for the better class of bituminous paint product such material is undesirable. Petroleum bitumens seldom contain either mineral matter or non-mineral matter insoluble in carbon bisulphide. The petroleum naphtha test is a supporting test mostly used for identification purposes. In general the solubility of the petroleum bitumens runs parallel with their hardness, the harder the material the less readily it dissolves.

(iv) **Mineral Ash Content.** The nature and quantity of the mineral ash may serve to identify the origin of the bituminous material.

(v) **Saponification Test.** This test, together with the further examinations of the saponifiable and unsaponifiable components, is especially valuable for examining mixtures of bituminous material with drying oils, and pitches, especially stearin pitch.

The interpretation of the above tests will actually turn upon what indications are gathered in a preliminary examination as to whether the material examined is a simple or blended product. It is not always possible to use a single bituminous material if a certain combination of characteristics is required, and then recourse must be had to blending. For the manufacture of bituminous paint products, however, this process of blending is best left as far as possible to the primary producer of the bituminous material. Even then in dealing with mixtures it is always necessary to bear in mind the 'compatibility' factor, to which some reference has already been made, for this above everything else determines the quality of the performance of bituminous paint products. It is not only the blending of different types of bitumen (and a perfect blending means much more than merely melting or running together), but the blending of the bitumen with the other components of the mix. Indeed, some of the additions commonly made to bitumens, notably rosin, rosin oil, rosin pitch, and particularly animal and vegetable oils, are used almost as much for their fluxing action as for their more specific qualities.

No details are given for carrying out the above tests, which are all standard tests applied to bituminous materials and are fully described elsewhere under the appropriate section.

IV. MANUFACTURE OF BITUMINOUS PAINTS

(*a*) Media

To prepare a solution of bitumen in a solvent is a comparatively simple matter; many bituminous materials can be 'cut' cold, but in general it is easier to use heat either by melting the bitumen at the lowest possible temperature and adding the solvent, or by stirring the bitumen and solvent together in a closed vessel suitably heated to some temperature below the boiling-point of the solvent. Some materials melt at so high a temperature that a fluxing operation is almost necessary.

The incorporation of oils and resins with bitumens is a much more serious matter, for the type of oil and the grade of resin to be used often determine the method of manufacture.

Obviously some solutions of bitumen in solvent can be mixed off with oil or varnish material, but some degree of heating is usually necessary to ensure miscibility with oils, and the plant necessary for these processes is something more than a mere mixing vessel. Mention has already been made of the dangers of heating bitumens, and there is no doubt that by so doing considerable changes occur in chemical constitution, changes which are reflected in the solubility and colour density. Oxidation and carbonization can also occur, and long before there is real carbonization or cracking the free-carbon content can increase enormously with an aggravation of the drying problem (if oil be present) later on. Even without any increase in the free-carbon content (which will be highly reactive and adsorptive material) the bitumen, especially if gilsonite, progressively adsorbs the drying metallic compound previously added to the oil/resin part of the medium. In practice one is able to obtain good drying property for some days after manufacture, but the drying time progressively lengthens until after, say, 3 months it may be increased from 8 hours to as many days or more. It is necessary, therefore, to satisfy the adsorptive capacity of the gilsonite before the adjustment is made as to drier content in order to control the drying period. It is equally obvious that any excess of free drier material in the oil component beyond the amount required is extremely harmful, although adsorbed drier material removed from the oil seems to be comparatively innocuous.

Details of the method of manufacture and the temperature to be used will vary with the material, but the general rule will apply, viz. as little heat as possible and for the shortest possible time necessary to achieve the desired process. When bitumen is to be melted alone, heat should be applied gently, and if mixed bitumens are used, the lowest melting-point material should be taken first, and other material added gradually so that liquid material always remains in the vessel.

The method of manufacture of bitumen/oil compositions closely follows ordinary varnish-making procedure. If it is a question of fluxing together bitumen and previously heat-treated oil, the temperature range should be about 220–240° C. and never exceed 260° C. It is better to incorporate such driers as are required in the oil before admixture with the bitumen, and, of course, there are several ways of varying the procedure in the manner of bringing the components together. For the sake of cheapness or convenience, or both, it is not unusual to flux the raw oils with the bitumen and to 'body' up the mass by subsequent heating, but in that case it is necessary to raise the temperature up to 260° or even 280° C. for a time, but this procedure is not recommended. After cooling to 200° C., or thereabouts, the driers are added, and at 150° C., or thereabouts, the solvent or thinner material is added. Alternatively part of the thickening of the oil may be carried out before mixing with the bitumen and part afterwards by the use of higher temperatures in the manner indicated.

If a resin is also to be incorporated into the mix, the most useful and satisfactory procedure is to flux the resin and oil together, following standard varnish-making practice, before mixing with the bitumen.

When tung oil is used in the mix, even as part only of the oil content, the technique of manufacture needs a greater measure of control owing to the sensitivity of tung oil to heat and its extraordinary capacity for rapid gelation under heat.

If the tendency of tung-oil products to produce frosted and wrinkled films is to be avoided, it is essential that the oil shall be heated to a certain minimum extent, say, about 40 minutes at 250° C. or for shorter periods at higher temperatures. On the other hand, the oil must not be cooked to the point of gelation, or a non-homogeneous product will result and become obvious on painting out.

The presence of resins generally, and particularly colophony (rosin) helps considerably with the handling of tung-oil mixes because these resins greatly retard gelation. A high proportion of an oil such as linseed oil, restrains gelation according to the amount added. The bituminous matter alone cannot be depended upon to restrain sufficiently the gelating tendencies of tung oil, if only for the reason that tung oil must be heated before it comes into contact with the bitumen. Quite a number of other methods are used for restraining the gelation of tung oil, such as heating with small quantities of sulphur, selenium, certain substituted phenols, and arsenious oxide.

It is also quite practicable to heat tung oil so rapidly as to carry it beyond the critical gelation period, and thus produce an oily product which will no longer gel. If this superheating is carried to excess the material may lack drying qualities, but with care this condition can be avoided. Further, additions of this superheated oil can be used to restrain the gelation of further quantities of tung oil.

The effect of quite small proportions of tung oil in a bituminous/oil product can be observed in the quality of the film produced, and there is good reason to believe that the optimum ratio of the linseed/tung oil mix, having regard to both performance value and cost, is about 30% tung oil.

(*b*) Special Media

Whilst the quantity of material made, which properly falls into this classification, may be very small, its interest is large. The development of phenol formaldehyde and alkyd type synthetic resins has been mentioned earlier; they are already important constituents of bituminous paint products. For various reasons, most interest has been shown in the phenolic types of resins, but a typical air-drying resin of the oil modified glycerol phthalate type may be used wholly or in part in substitution of the ordinary oil or varnish component of the bituminous varnish and form as much as 60% of the solid matter in the film.

Shellac was at one time incorporated with bituminous media in order to improve the drying quality and to harden the film.

There are various references in the literature to the use of other materials in combination with bitumen in paint in order to confer some special quality; for example, a proportion of gutta-percha and depolymerized, soft, vulcanized rubber incorporated with bitumen is said to confer unusual acid resistance.

Straight rubber/bitumen mixtures are difficult to produce except by melting together, and comparatively small amounts of rubber soon decrease the flow properties of the product, but chlorinated rubber is readily soluble and compatible with oil and bitumen and is used to produce media for special purposes, among other things to give resistance to chemicals and electrical stress.

(*c*) Pigmented Products

It has already been pointed out that bituminous paints may be produced by hot or cold processes, and the type of the product will determine the manner in which the incorporation of the pigment is carried out. Not infrequently it suffices to mix the pigment with the medium whilst the latter is still hot. The alternative is to grind the pigments with the medium in paste form (in a ball mill or other standard type of paint-grinding machine), afterwards thinning the paste to brushing consistency. This process is likely to yield a better ground product, and is usually carried out on the finer products such as are known as bituminous enamels.

(*d*) Emulsions

In the manufacture of emulsion paints the bituminous material is dispersed in water. This condition is promoted by small quantities of emulsifying or dispersing agents which may also act as stabilizing agents for the emulsion when formed, functioning as protective colloids. The list of materials which may be used or whose use has been protected by patent is very large, but the common ones are soaps of all kinds, sulphonated oils, the silicates of sodium and potassium, proteins (such as glue and casein), and colloidal clays, either alone or in admixture.

A convenient method of manufacture is to pour the molten bitumen gradually with agitation into warm water already containing the emulsifying agent. Alternatively, the warm water (at a temperature usually between 50 and 80° C.) can be stirred into the molten bitumen to which has already been added the soap or potassium silicate or other emulsifying agent. This simple agitation method, carried out in suitable kettles, is suitable for material which can be melted below the boiling-point of water, or if used in a cold process, for material which can be previously and easily broken up into a free powder.

Of the other types of apparatus employed for the manufacture of bituminous emulsions the best known are colloid mills and homogenizers. These colloid mills carry moving parts revolving at high speed in fairly close contact so disposed as to submit the particles passing through the mill to considerable shearing stress. Colloid mills are well suited to the dispersion of previously ground material and also to the dispersion of liquid and heated material.

Very wide variation is found in the bitumen content of emulsions according to the desired application, but many range about 50%, and frequently the amount of emulsifying agent may reach 10% or more. For paintwork the bitumen is often plasticized with such material as stearin pitch for straight work, or with oil varnish if the product is to be coloured. The pigmentation of bituminous emulsion is carried out by adding the pigment as an aqueous paste, some of the water from the emulsion having been reserved for the purpose. In this way the pigment is maintained water wet, a most important consideration.

Emulsion films do not flow or sag under heat in the same way as do ordinary bituminous films. The reason is that emulsion films acquire an artificial rigidity by structure; and by way of explanation it is convenient to consider the analogy between bituminous films so produced and the films of oil-bound water paints.

A bituminous emulsion is very like water paint, which as a rule can be described as a pigmented dispersion of oil or varnish in an aqueous solution of glue or casein. The pigment, mainly water-wet, rides at the interface between the globules of the disperse phase and the continuous medium, and has very definite functions in maintaining stability of the paint and determining the characteristics of the films produced therefrom. Similarly, some proportion of solid matter is essential for the production of bituminous emulsions, whether they are to be used for road treatments or paint purposes (quite apart from emulsifying agents like soaps which have another special function). In the absence of a definite pigment, bentonite is sometimes used to the extent of 4 or 5%, at most, measured on the bitumen content.

To continue the analogy with water paint, when a water-paint film dries it can do one of three things:

(1) dry with the same structure as the wet film, or
(2) the emulsion may reverse, i.e. become water-in-oil instead of oil-in-water type and dry as such, or
(3) the phases may separate, one of which will dry as oil or varnish and the other as pigmented glue or casein.

It is difficult to trace any such changes experimentally, but from study of dried films there is no evidence of emulsion break or of separation of the phases as characteristic changes. Emulsion break does occur sometimes whilst the paint is being brushed out, but in that case the film is unsatisfactory and the paint useless. The application and drying of bituminous emulsions presumably follows a parallel course; moderately pigmented bituminous emulsions can be worked with the brush quite freely, but emulsions containing the minimum amount of solid matter are easily broken. Once painted out, the free evaporation of water induces a rapid set in the film, which, having a high yield value, stays in position, even if very thick, and does not sag or flow.

Now, as the water evaporates, the droplets of bitumen must settle down on to the support. Do these droplets coalesce and so form a continuous film? If they do, the film should not be distinguishable from other types of bituminous films (deposited by solvent evaporation), but it is known that films formed from bituminous emulsions do not flow (at least not for a long time). This resistance to flow is dependent upon the film having structure, a quality which arises from the arrangement of the solid material in the film, presumably, as it originally existed in the fluid material. If the structure persists, the original droplets must remain as such; if the droplets coalesce, the structure would be lost and the film would no longer resist flow.

It is often noticed that bituminous emulsion films do flow after a time, and this is commonly supposed to indicate the complete drying out of the film. This view is only true in part; it is not the loss of water as such that matters, but the fact that with complete drying out the originally water-wet solid tends to become oil-wet, and so pass into the body of the bituminous material. The barrier between the globules thus being broken down, the film acquires the characteristics of the ordinary type.

V. APPLICATIONS OF BITUMINOUS PAINTS AND EMULSIONS

(*a*) General Uses

Considering the many varieties of bituminous paint compositions which have been mentioned in this article, and that each has been devised more or less to suit some special need or conditions of use, it is obvious that any attempt to make a complete survey of the applications of bituminous paints would soon degenerate into a mere catalogue of little value. Bitumens have special properties which in some measure they impart to bituminous paint films, particularly elasticity, resistance to water, acid, alkali, and electrical stress, and a consideration of these properties in relation to use on metal, wood, or concrete, on ships, and in the production of electrical gear will suffice to cover the whole field of application in a general way.

One considerable weakness of bituminous paint compositions is their low resistance to abrasion, so that it is often necessary to depend upon using a film of considerable thickness. Pigmentation or the use of filling material will increase resistance to abrasion, but if this process is carried beyond a certain point the material obviously becomes more like a plastic bituminous cement or coating compound than a paint suitable for brush application. Likewise bituminous paints will not give satisfaction if exposed to materials such as turpentine or petroleum (directly or as vapour) which can exercise solvent action on the bitumen.

Once a structure has been painted with bituminous paint it is unsafe to apply ordinary paint without using an intermediate or sealing coat, such as shellac varnish, a proceeding which is not always satisfactory in the long run. Although ageing and exposure of bituminous films result in loss of solubility through oxidation, some softening of the film during the application of new paint is inevitable, resulting in 'bleeding' and an injurious action on the drying of the superimposed layer of oil paint. On the other hand, bituminous paints can be successfully applied over old dried films of ordinary paint and varnish, so long as the old films are not peptized by the solvent.

Bituminous paints are not particularly recommended for use on wood, as the heavy and somewhat irregular adsorption of the liquid material tends to spoil the appearance of the film, and second-coat application to get a good finish is not easy. The heavy adsorption and retention of solvent by wood often results in trouble developing at a later stage, especially if the wood is highly resinous.

(*b*) Anti-corrosive Uses

Bituminous paints and coatings have rightly been considered as having special importance from the point of view of rust and corrosion prevention; indeed, they are mainly prepared for application to iron and steel as anti-corrosive preparations. Wherein lies the special qualities of bitumen in this respect, and what is the cause of failure when failure does occur? Briefly it may be said that the value of bitumen as an anti-corrosive material lies in its neutrality (except in the case of tars and certain pitches) and capacity to exclude both air and water from the metal surface. This bald statement, of course, requires qualification and amplification, but, unfortunately, knowledge of the mechanism of the protective action of bitumen is even less developed than that of other materials. In considering the problem of corrosion in relation to bitumen, one must remember that there are two principals—the metal and the paint. Then follow the obvious questions: Are the seeds of corrosion actively present in the metal surface before painting? Will the tendency to develop corrosion be crushed or inhibited by the paint? What about the electrical 'stray currents' which work such havoc in underground structures? What about the atmosphere, for neutral atmospheric corrosion is different from that due to acid atmosphere?

For a fuller consideration of these questions reference should be made to the general article on 'Principles of Corrosion'. Here the fundamentals of the matter can be treated only in a superficial manner, for the purpose of this article is to say what experience has found with bituminous coatings as anti-corrosive materials with some indication as to why certain results have been obtained.

In general, bituminous paints will give fair service on ironwork exposed to ordinary weathering, provided the material is properly compounded. The great advantage of bitumen is its pronounced water resistance, far above that of most paint films, but this of itself is not sufficient to maintain high anti-corrosive quality, for the water resistance is lessened very quickly by exposure. The bituminous film must not show pinholes or other breaks permitting access of the atmosphere, nor must it develop the large-scale cracking for which the material has in time past been notorious. The adhesion of the film must be high so that it will not flake or chip away from the metal as the result of accidental blows. Moreover, strong adhesion has a marked effect in promoting that resistance to corrosion under the film which culminates often enough in detaching paint in large pieces, particularly from metal which has been irregularly descaled and exposed to the atmosphere for a considerable time before painting. If the innate anti-corrosive capacity of bitumen is due, as many suppose, to the presence of certain components having a specific inhibiting property, it is most important that they should be brought into intimate contact with the metal surface, and adhesion is in this respect a most important quality.

In obtaining maximum anti-corrosive quality there must be suitable choice of the bitumen, or the bitumen mixture, and particularly of the plasticizer used. The chosen bitumen should have low acid value, a minimum ash content, and be so compounded with oils and soft material such as stearin pitch, and possibly pigment, as to give good adhesion with no cracking on exposure. Hence the use of bituminous varnishes and japans which suffer less than the straight bituminous materials from general weathering faults, such as loss of colour and gloss, oxidation leading to disintegration of the surface, and lessened water resistance. Stoved products usually give better general performance than air-dried products, and this is particularly noticeable where damp conditions obtain.

Naturally the relative value of different films will depend on the oil length of the material. Large proportions of heat-treated linseed and tung oils increase the elasticity, adhesion, and general durability at the expense of chemical and water resistance.

The question often arises as to the desirability of applying bituminous material over iron already coated with red lead. The peculiar and valuable properties of red lead as a rust inhibitor are well known, and such a priming coat is often applied to steel work at the rolling mill. Experiment shows that provided the red-lead film contains the minimum amount of oil and is hard and roughened sufficiently by weathering or otherwise, no particular danger need be anticipated from a subsequent application of a bituminous coat, especially if fairly long in oil. On the other hand, fresh fatty coats of red-lead paint give poor anchorage to bituminous material (probably due to the peptizing action of solvent on the priming coat), leading on exposure to movements between the coats, cracking, and flaking away. Bituminous emulsions, as they avoid any solvent action on the priming coat, can be applied very successfully over red-lead coatings of all ages and conditions, and indeed bituminous emulsions can be applied successfully to iron direct. The spreading of the bitumen is facilitated in the emulsified form, and the wetting power of bitumen for iron being greater than that of water, probably avoids undue metal/water contact during drying.

The use of bituminous products on submerged steel has been the subject of much debate in recent years, but there is little doubt that when reports have been adverse the composition used could be criticized as having been unsuitable from the beginning.

The problem of protecting iron subjected to intermittent immersion in water is particularly difficult at all times; it is a more serious problem than providing protection under conditions of complete immersion. Obviously one is forced to a compromise between water resistance as such and weathering resistance. Sooner or later, depending on the film, its quality, thickness, manner of decomposition, and rate of loss by water washing and corrosion, cracks will permit access of water to the metal; thereafter the rusting effect is not within the control of the bituminous film.

Pigmentation of the bituminous material, particularly with aluminium powder, is an admirable method of prolonging the life of the film under these difficult conditions; it mitigates the sun effect, produces a greater resistance to the scouring action of the water, and materially improves the life of the film. However, apart from the use of aluminium, compositions containing tung oil and gilsonite have been used very successfully on the wind and water line of ships, and, in admixture with fatty acid pitch, as the base of anti-fouling paints.

Bituminous paints have also been found very successful for painting the insides of water tanks.

The admittedly high resistance of bitumens, especially the harder types, to the attack of acids, alkalis, and chemicals generally leads to obvious uses for bituminous paint compositions in chemical works and the like for the protection of the structure, tanks, and floors. One example of use which is perhaps unusual is the successful painting of steel lorries used for the carriage of salted hides from the docks to tanneries. Ordinary oil-base paints are destroyed very quickly as they are permeable to salt solution, with the result that the steel not only corrodes very rapidly but stains the hides. Whatever the paint, once the salt solution penetrates the coating, corrosion will be rapidly stimulated, causing blisters and throwing off the paint in patches. Straight bituminous paint admirably resists the salt, but does not withstand the vibration and hard usage, for it flakes away in places. The requirement is met by a bituminous product so nicely balanced in its composition that there is sufficient bitumen to give impermeability and chemical resistance and sufficient plasticizer to give adhesion and mechanical resistance to shock and hard wear.

(*c*) Uses as Emulsions

Bituminous emulsion paints are now enjoying considerable general use; mention has already been made of bituminous emulsions in anti-corrosion work and of aluminium paints on a bituminous base for which purpose the emulsion form is suitable. Bituminous emulsions can also be coloured by pigment, and the pigment particles, water-wet but lying at the interface, shroud the bitumen particles to some extent and thereby give the product a clean shade if the pigment is a strong staining colour. Films made from bituminous emulsion are less susceptible to heat than similar bitumen applied in ordinary solvents, with the result that emulsion films do not flow and sag on exposure to the sun as do the other type of bituminous films. However, the principal use of bituminous emulsion paints is for application to damp walls, fresh concrete, and the like, whereby good adhesion is obtained between the damp surface and the bituminous film.

(*d*) Electrical Uses

The use of bituminous products for electrical work is well known, both as insulating varnish and as filling compounds and the like. The use of bitumen for this work is dependent first upon suitable electrical properties, high dielectric strength, &c., but also upon its resistance to moisture, a most important factor in insulation. The disadvantage of bitumen in electrical work lies in its susceptibility to mineral oil. Some mitigation of this trouble is obtained by using bituminous varnishes and japans containing a substantial proportion of oxidized vegetable oil which when stoved yield hard films capable of resisting the attack of mineral oil fairly well.

Varnishes such as those described for electrical purposes are also used for impregnation of papers, tapes, boards, brake linings, and many other purposes.

VI. TESTING OF BITUMINOUS PAINT COMPOSITIONS

The value of the product and the devising of tests for the determination of the same must depend upon its nature and the purposes for which it is intended to be used.

The first group of tests to be applied can be properly described as *tests relating to composition*:

(*a*) Non-volatile Matter

(1) Bituminous content, type and quantity.
(2) Oil content, if any, type and quantity.
(3) Pigment content, if any, type and quantity.
(4) Presence or absence of specified materials.

(*b*) Volatile Matter

Type, boiling range, and quantity.

(*c*) Characteristics

Such as flash-point, specific gravity, viscosity, miscibility with oil, &c.

The exact requirements of these tests will vary widely according to circumstances, but they are of the nature of specification tests, for details of which various British Standard Specifications may be consulted.

Sometimes it is necessary to make a more detailed chemical examination of the material, and that being so, indication may be given as to the manner of carrying out such a scheme of test, although for full details reference should be made to standard works.

The first step is to separate
(1) solvent,
(2) pigment or filler,
(3) bituminous base or medium.

The most obvious method of removing solvent from bituminous paint products is ordinary steam distillation. Definite forms of apparatus have been devised for specification purposes. When the distillation is finished, the quantity of distillate can be measured and examined by chemical and other means, such as the determination of specific gravity, refractive index, flash-point, distillation range, as required for identification.

Certain care has to be taken in respect of water-soluble matter which may otherwise be lost. If the distillate does not separate readily from the water, this separation can be facilitated by the addition of sodium chloride, the use of which will result in a clear separation of the two layers.

The clean separation of pigment, if any, is a matter of repeated extraction with benzol or other solvent until the pigment is free from traces of the vehicle. A centrifuge or a Soxhlet thimble may be used. If no pigments or fillers are present, the vehicle is examined directly after the removal of the solvent. If oxidizable substances are present, any evaporation must be carried out in a neutral atmosphere.

After removal of volatile matter the medium is weighed, and is then saponified by refluxing for an hour with a 20% solution of caustic potash in methyl alcohol (5 c.c. per g. of medium) and an equal volume of benzene. The saponified mixture is diluted with about twice its volume of 1% potassium chloride which serves to reduce the tendency to emulsification. The unsaponifiable matter is next extracted by means of benzene, the extract is dried by means of sodium sulphate, the benzene evaporated, and the residue weighed as unsaponifiable matter and its nature determined by examination of its physical and chemical properties. In this connexion it should be noted that insoluble mineral matter and free carbon have already been removed with the pigment. In addition to bituminous materials, the unsaponifiable matter may contain rubber, chlorinated rubber, coumarone and other unsaponifiable synthetic resins, lanolin, petroleum products such as vaseline and paraffin wax, alcohols from saponifiable waxes, and unsaponifiable matter from natural resins, should any of these materials be present. Separation is best effected by extraction with suitable solvents.

The aqueous layer after removing the unsaponifiable matter is acidified and subjected to steam distillation. The presence of phenols in the distillate is an indication of the presence of a tar such as coal, wood or bone tar or pitch, or rosin pitch. Mineral bitumens, such as gilsonite, and fatty acid pitches, such as stearin pitch, do not yield any phenols.

The residue after removal of the phenols is allowed to cool and extracted with ether. The ether extract contains any fatty and resin acids present in the original material. These are separated by any of the standard esterification processes, of which Wolff's method [2] may be recommended, and the separated fractions weighed. The esterified fatty acid fraction may contain esters of oil acids, which can be identified by determination of their refractive index, hexabromide value, iodine value, &c., and of acids derived from fatty acid pitches; the pitch acids are distinguished from the oil acids by their high lactone value (> 25), Kramer-Sarnow fusing-point (> 25° C.), and hardness (> 5·0 at 25° C.) and darker colour. The resin acids may be identified by means of their colour reactions, acid value, &c.

The aqueous residue after extraction of the fatty and resin acids should be tested for glycerol. If this is present, the original material contains vegetable or animal oil. If fatty acid pitch has been shown to be absent, the proportion of oil present may be calculated by multiplying the weight of fatty acid esters by the factor 0·95. If the presence of fatty acid pitch is known or suspected, the glycerol should be determined quantitatively, and the quantity found multiplied by 10 to give the weight of oil present in the sample. From this value the weight of oil and esters may be calculated in order to ascertain whether the fatty ester fraction consists entirely of esters of oil acids, or whether, alternatively, esters of fatty acid pitch acids are present. The small percentage of glycerol present in fatty acid pitch may be ignored in this calculation.

The aqueous liquid may contain, in addition to glycerol, salts of any metals present in the material under examination. Likely metals are lead, manganese, and cobalt, present as oil driers, and zinc, calcium, and magnesium, present as hardening agents for rosin. These may be detected by the ordinary methods of qualitative analysis, and, if necessary, determined quantitatively in aliquot portions of the solution. Otherwise the examination of the base material follows the scheme outlined in the sections dealing with selection of the components.

The second group of tests to be applied may be described as *tests relating to general performance* of the product in use:

(*d*) Workability or Flow.
(*e*) Drying Time.
(*f*) Covering Power and Hiding Power.

(*d*) Workability or Flow

Much can be learned from the report of a skilled painter working under normal conditions as to the brushing qualities of the material.

In those cases where the material is to be applied by spray or by dipping, the procedure must be modified accordingly. Japans, for example, are frequently applied by dipping, and it is customary to measure by weighing the film thickness left on suitable paper or metal strip when withdrawn from the dipping bath at a definite rate and suspended vertically to drain and dry.

(*e*) Drying Time

The important points to notice are the time which elapses before a painted-out film just loses its tack and the time when the film becomes firm and tough.

A useful indication as to the manner of carrying out drying-time tests is given in British Standard Specifications for Varnishes. The test requires that the varnish shall become surface dry in not more than 6 hours and hard dry in not more than 18 hours, when tested in the following manner.

'The varnish shall be brushed on a tinned iron panel of convenient size so as to produce a dry film weighing approximately ¾ oz. per sq. yd. (25·5 g. per sq. in.). The varnished panel shall then be placed in a vertical position in a well-ventilated room at 60° F. (15·6° C.). The varnished surface shall be illuminated by diffused daylight for at least 6 hours during the drying period, and care shall be taken to protect it from exposure to direct sunlight.

'By the term "surface dry" is understood such a condition that clean, dry, silver sand (graded so as to pass a No. 52 B.S. Sieve, but to be retained on a No. 100 B.S. Sieve (B.S.S. No. 410) which has been sprinkled on to the surface of the varnish film and allowed to remain there for about 1 minute, can be removed, without injury to the varnish film, by means of a camel-hair brush.

'By the term "hard dry" is understood such a condition that a second coat of the varnish can be satisfactorily applied after slight rubbing down.'

Mechanical methods have been developed and used for carrying out the same test in an automatic manner.

For electrical work a rather more elaborate procedure is usually required, such as will be found described in B.S.S. No. 514.

(*f*) Covering Power and Hiding Power

The covering or spreading power is the amount of material used in normal application, expressed as gallons or pounds per unit area covered, and is determined by weighing the panel before and after application. Hiding power may be defined as obliterating power, and hiding thickness is the minimum thickness of paint which will obliterate beyond recognition any background upon which it may be spread. Actually hiding power regarded as a measurement of opacity or transparency of the film can be directly determined without the intervention of any background. In any case the determination of this figure is a matter of instrumental measurement, and the various methods for determining the same should be consulted in the standard works on paint technology.

Finally, it is necessary to devise *tests* for the examination and determination of the *performance value* of the films themselves. The tests to which the finished films are subjected must depend upon the use to which they are to be put, such as the determination of water absorption, water permeability, resistance to acids, alkalis, and oil, elasticity, weathering, electrical properties, &c.

(*g*) Water Absorption

Except for electrical purposes, it is sufficient to study the condition of the dried and possibly stoved film after immersion in water for 24 hours. High absorption will often cause a dulled surface and loss of adhesion, and in the case of material used as insulating varnish, loss of electrical strength. More elaborate methods for determining the permeability of films to water can be used if necessary.

In B.S.S. No. 514 for Baking Insulating Varnish (Bitumen type) the resistance to moisture is determined by an electric strength test on varnished paper at 20° C., which under defined conditions of test shall not be less than 500 volts per mil. The conditions of test are fully described in the specification.

(*h*) Resistance to Acids, Alkalis, and Oil

The dried film is subjected to the action of sulphuric acid, and, if necessary, other acids, and to the action of sodium hydroxide for a period of hours, or in some cases days, depending upon the strength of the acid or alkali used. In the case of the sulphuric acid test, American practice requires the dried film to withstand 33% acid for 6 hours, but it is rather unusual to require acid of such strength, 20% being probably the limit strength used in the ordinary way.

Paints made from coal-tar pitches are much less resistant to strong acids than paints made from petroleum bitumens and natural asphalts.

The usual method of testing resistance to oil is immersion in transformer oil at 100° C. for 24 hours. The bituminous varnish should not be softened sufficiently to produce a stain when rubbed with a white cloth.

(*j*) Elasticity and Ageing Test

This type of test is of special value in the case of baking japans and bituminous varnishes. The material is applied to one side of strips of clean copper foil (6 in. × 2 in. × 10 mil thick), and when dry bent over a rod ⅛ in. in diameter. The exact details of the test will naturally vary with the use to which the material is put and the performance required of it; as an example B.S.S. 514 for Baking Insulating Varnish (Bitumen type) requires the following:

'The ageing test shall be carried out on a strip of varnished copper foil 10 mils thick and about 6 in. by 2 in. The foil shall be sufficiently flexible to withstand, without cracking, 30 bends (15 in each direction) round a rod ⅛ in. diameter.... The surface of the foil must be free from grease, and this can be secured by rubbing it with cotton-wool dipped in benzole.

'The varnish shall be applied, to one side of the foil only, by flowing over the clean surface of the foil so as to produce a uniform film. The varnished foil shall be allowed to dry in dust-free air in an upright position for half an hour at a temperature between 15° C. and 25° C. It shall then be stoved for 2 hours at a temperature between 100° C. and 105° C., and the air content of the oven shall be changed not less than three times per hour. A second coat of varnish shall then be applied, and the specimen shall be drained and stoved as before. When the specimen is being drained and stoved the second time, it shall be placed in the reverse direction to that employed for the first time.

'On removal from the oven the varnished foil shall be kept for 1 hour at a temperature between 15° C. and 25° C., and the thickness of the film shall then be measured. The film shall be not less than 5 mils or more than 7 mils thick; if less than 5 mils further coats of varnish shall be applied as before, the final coat being stoved until the varnish is dry; the stoving period for this coat shall not exceed 8 hours.

'The varnished foil shall be heated for 100 hours at a temperature between 115° C. and 120° C., the air content of the oven being changed not less than three times per hour. At the end of this period the varnished foil shall be kept at room temperature (15–25° C.) for 1 hour.

'The foil, with the varnish film outside, shall be bent double over a rod ⅛ in. diameter by means of the apparatus shown in Fig. 2, the rate of bending being such that the complete bend of 180° is performed in 2 seconds. The bending test shall be made at two places on the sample, and shall be carried out at room temperature (15–25° C.).

Note.—Some samples of copper foil themselves show minute hair cracks, and, when cracking is observed, care must be taken to ensure it is in the varnish.'

(*k*) Weathering

The determination of the performance value of paint and varnish films, both by natural weathering and artificially accelerated weathering, is an everyday procedure.

Bituminous products are no exception to the general rule, namely, that they change both physically and chemically on exposure to the air and atmospheric influences.

It is possible to correlate or connect the results of exposing films of bituminous material with changes due to oxidation, polymerization in the mass of the material itself, and the leaching out of water-soluble substances from the body of the material.

Whether it is possible to correlate the performance of films naturally exposed to those weathered artificially is a debatable question perhaps, but no doubt experience and care in judgement permits useful results to be obtained from accelerated tests. Without entering into the details of the methods of carrying out such tests, they usually consist of a cycle of operations involving exposure to light from carbon arcs or mercury-vapour lamps, rain-water, and changes in temperature down to freezing-point. These processes simulate the conditions of natural exposure and lead to changes in the water content of the film and movement of one layer of the bituminous material over another, such as the upper crust sliding over the softer sub-stratum leading the checking, wrinkling, and, in the end, cracking of the material. Cracking in the first stage may be very fine, only visible under the microscope, but, in the end, it may become very large and coarse.

Another test which is commonly applied to certain types of bituminous coatings is to spray with salt-water. No elaborate arrangements are necessary, it usually being sufficient to suspend the panels in a cupboard or small room into which a mist of salt-water is projected. The break-down of films can be tested by an electrical conductivity method in which the panels are spotted by a conducting solution, and where there is a break-through of the film or a crack on its surface the position is disclosed by the completion of a suitably arranged electric circuit.

Exposure of bituminous films, especially to light, leads to marked changes in the state of the bitumen, which becomes lighter in colour, less soluble, more heavily carbonized, rather harder, and less resistant to moisture. Part of these changes are due to loss of volatile material by evaporation, partly to oxidation, and partly to polymerization effects.

The extent of these changes, which are indicated by altered appearance of the bituminous film, particularly colour change, loss of gloss, powdered surface, cracking, flaking, and corrosion (if on iron panels), is the inverse measure of the durability of the material against weathering influences.

REFERENCES

1. MACK, C. *J. Phys. Chem.* **36**, 2912 (1932).
2. WOLFF, H. *Farben-Ztg.* **26**, 2208 (1921).
3. WOLFF, H., and SCHOLZE, E. *Chem. Ztg.* **38**, 382 (1914).

THE COLLOIDAL STRUCTURE OF BITUMENS

By F. J. NELLENSTEYN, Ph.D.

Government Road Laboratory, The Hague (Holland)

At the beginning of this century Richardson [18, 1906] published his researches on Trinidad asphalt; henceforth this field was opened for colloid chemistry. The principal fact is the application of the ultra-microscope to asphalts, i.e. mixtures of asphaltic bitumens and fine mineral powders, so-called 'fillers'. Attention is especially drawn to these 'colloidal fillers' in Trinidad asphalt, but the problem of the asphaltic bitumen as a colloidal system is neglected. Richardson's ultra-microscopical researches are continued by E. C. Lord [5, 1919].

The colloid chemistry of asphaltic bitumen has been especially studied by the author and his co-workers [12, 1932].

The nomenclature followed here is fixed by the Permanent International Association of Road Congresses. The principal definitions are:

Bitumens. Mixtures of natural or pyrogenous origin or combinations of both (frequently accompanied by their non-metallic derivatives) which can be gaseous liquid, semi-solid, or solid, and which are completely soluble in carbon disulphide.

Asphaltic Bitumen. Natural or naturally occurring bitumen or bitumen prepared from natural hydrocarbons by distillation or oxidation or cracking; solid or viscous, containing a low percentage of volatile products; possessing characteristic agglomerating properties, and substantially soluble in carbon disulphide.

Tar. A bituminous product viscous or liquid resulting from the destructive distillation of carbonaceous materials.

Asphalt. Natural or mechanical mixtures in which the asphaltic bitumen is associated with inert mineral matter.

Although many controversies remain, I give the following survey of theoretical views, which are more or less generally accepted:

The Constitution of Asphaltic Bitumens, Asphalts, and Allied Systems, e.g. Tars.

These systems are highly protected lyophobe sols. As such they contain three principal groups of components [9, 1928]:

(1) the medium;
(2) a lyophile part: the protective bodies;
(3) a lyophobe part: the ultramicrons and microns.

The medium may be characterized as a mineral lubricating oil in asphaltic bitumens, and asphalts, and aromatic oils in tars.

The protective bodies generally are highly unsaturated hydrocarbons, often with a high sulphur content. In their physical properties these bodies resemble resins.

The nature of the lyophobe part, the ultramicrons and microns, has been a subject of much discussion. I shall revert to these controversies later.

Stability Conditions. The disperse phase of these systems is formed by the last two groups, the protective bodies and the ultramicrons or microns, these groups being the constituents of the asphaltic bitumen-, asphalt-, or tarmicelles. The stability of these systems in the first place depends upon the relation between the micelles and the medium. Changes in this stability caused by flocculative and peptizing agents are known as the phenomena of the 'reversible flocculation'. Flocculated micelles may be repeptized by peptizing agents, as long as the micelles remain intact, but if the micelle itself is destroyed, it cannot be repeptized directly by peptizing agents; in this case 'irreversible flocculation' takes place.

The reversible flocculation of asphaltic bitumen and asphalt conforms to the surface-tension rule, given by the author [9, 1928].

When mixing asphaltic bitumen with liquids, which are totally miscible with the medium and the protective bodies of this bitumen, flocculation occurs when the liquid has a surface tension below 24 dynes per cm. at 25° C.; if the surface tension is higher than 26 dynes per cm. total peptization takes place, while in the intermediate zone of 24–26 dynes per cm., flocculation or peptization depends upon the more or less stable character of the micelle.

The following table shows the relation of flocculating and peptizing properties of different liquids, which are totally miscible with the medium and protective bodies of asphaltic bitumen:

Liquid	*Surface tension at 25° C.*	
Pentane	13·5	Flocculating reagents
Ether	16·7	
n-Hexane	17·0	
n-Heptane	18·6	
Carbon tetrachloride	25·4	Intermediate zone
Cyclohexane	25·7	
Chloroform	26·2	Peptizing reagents
Benzene	27·7	
Toluene	28·4	
p-Xylene	29·1	
Carbon disulphide	30·6	
Pyridine	34·9	
Nitrobenzene	42·5	

Carbon tetrachloride, as a liquid of the intermediate zone, combines peptizing and flocculating properties. It is apt to flocculate especially when a less stable system has been formed; in practice this is caused by faults during distillation or blowing, or when road asphalt has been overheated during the mixing process. A slight decomposition of the micelle, not going so far, however, to the formation of 'free carbon', which is insoluble in carbon disulphide and other high surface-tension liquids, may be detected by adding carbon tetrachloride. This fact has already been stated by Richardson, but according to the generally accepted classic-organic views, he supposed the presence of special compounds, soluble in carbon disulphide but insoluble in carbon tetrachloride, which he called 'carbenes', and which should always indicate an inferior character of the asphaltic bitumen. According to the preceding consideration, the intermediate position of carbon tetrachloride between the *low surface-tension flocculating* liquids and the peptizing high surface-tension solvents *explains Richardson's reaction of the so-called carbenes simply as a reaction of a less stable asphaltic bitumen micelle.* The fact that the solubility of asphaltic bitumens principally depends upon two factors, i.e. surface tension and miscibility, is clearly demonstrated by the followting reaction.

Asphaltenes, precipitated from asphaltic bitumen with ether, and thoroughly washed with the same solvent, are practically insoluble in this liquid (surface-tension insolubility). These asphaltenes are also insoluble in aniline, which has a high surface tension (42 dynes per cm. at 25°) but is not miscible with the protective bodies in the asphaltenes. *In a mixture of both liquids containing equal parts of aniline and ether, these asphaltenes are totally soluble.* The value of the critical surface tension is related to the surface tension of the bitumen, which shows only slight variations for various asphaltic bitumens, but which is much higher for tars, about 8–10 dynes per cm. [16, 1930]. In consequence the critical surface tension, marking the limit between flocculative and peptizing reagents, has a much higher value than for asphaltic bitumens. Therefore liquids which are peptizing reagents for asphaltic bitumens may be flocculents for tars; this is the case with carbon disulphide and benzene. By these reagents 'free carbon' is precipitated from tars. It means, in accordance with practical experience, that the 'free carbon' belongs to the necessary compounds of a good tar.

While the reversible flocculation of the disperse phase of asphaltic bitumens and allied substances is a pure physical phenomenon, irreversible flocculation is mostly caused by chemical reactions, involving radical changes in the relation between the ultramicrons and the protective bodies; by these reactions the protected bodies are attacked and often destroyed. This causes a decreased stability and often a total destruction of the whole system.

A physical reaction causing irreversible flocculation is the exhaustive extraction with different liquids of successively increasing surface tension (gasoline of low boiling-point or ether, carbon tetrachloride, benzene). This reaction is theoretically important; it demonstrates that the degree of protection of the ultramicrons determines the solubility of the micelle and not a hypothetical chemical difference between products of different solubility, for which all sorts of names have been invented.

Microscopic and Ultramicroscopic Pictures of Asphaltic Bitumen, Natural and Artificial Asphalts, and Tars.

When investigating solutions of various bitumens microscopically or ultramicroscopically, solvents should be used of about the same surface tension as the bitumen. For asphaltic bitumens and asphalts carbon disulphide, for tars nitrobenzene or solvents of about the same surface tension and also totally miscible with the medium and the protective bodies of these systems are to be used.

There is a marked difference between the ultramicroscopic image of asphaltic bitumen and that of asphalt, but not between that of natural and artificial asphaltic bitumen or natural and artificial asphalt. Gilsonite, a natural, pure organic product, shows the same ultramicroscopic image as artificial asphaltic bitumen. This picture is not easily obtained; the best way is to use rather concentrated (10%) solutions and a powerful light source, while painstaking focusing and other precautions are required. The ultramicrons are very fine and not very luminous.

It has often been suggested that the inorganic compounds of natural asphalts have a special 'colloidal' character. However, there is no difference in the ultramicroscopic image of filtered solutions of natural asphalts and those of artificial asphalt mixtures if a fine filler has been added. The natural fillers are very fine, but not finer than some artificial ones. *The ultramicroscope clearly indicates that there is no principal difference between natural asphalts and artificial mixtures of asphaltic bitumens and fillers.*

Solutions of asphaltic bitumen are as a rule optically empty when examined with a microscope. Tar solutions, on the contrary, generally show a number of microns. The micron number, i.e. the number of microns in 1 mm. [3, 1913] of tar, counted in a 1% nitrobenzenic solution, has proved in practice to be a valuable indication as to the binding properties of the tar.

The foregoing gives an insight into the 'stabilized' aspects in this field of science, although many controversies remain. The first and most important question is that of *the nature of the micelle kernels.* Are these kernels highly polymerized hydrocarbons, sulphur or oxygen containing condensation products, or elementary carbon?

In the first and second case the kernels are supposed to be big molecules, the inner part consisting of carbon atoms, the outer part containing carbon, hydrogen, sulphur, and oxygen atoms. In the elementary carbon theory the carbon kernel is supposed to be protected by hydrogen, sulphur, and oxygen containing compounds, which compounds should be bound by adsorption. Although theoretically there is a principal difference between these views, attention may be drawn to the fact that in all these views an inner part of carbon is supposed to exist in these kernels; the external, hydrogen-containing part, may be connected to the internal carbon conglomerate by chemical bonds or by adsorption.

X-rays, applied according to Debye-Scherrer, show the presence of graphitic carbon in asphaltic bitumen, especially in the asphaltenes [11, 1933]. A reaction which may give an insight into the problem of the nature of the micelle kernels is the oxidation with $KMnO_4$ [8, 1925], especially of asphaltenes, which have been exposed to a long-continued extraction with solvents such as ether or gasoline. The oxidation products generally are the same as those obtained with active carbon, i.e. aromatic compounds (mellitic acid) and aliphatic products, which until now could not be identified but which are allied to the carbohydrates. From the X-ray image and this oxidation reaction it may be concluded that in a normal asphaltic bitumen graphitic carbon is certainly present. It is an open question whether the other allotropic modification of carbon, the diamond, may also occur in the cryptocrystalline form, and if this 'diamond-like' or aliphatic cryptocrystalline carbon is also present in the asphaltenes [7, 1925].

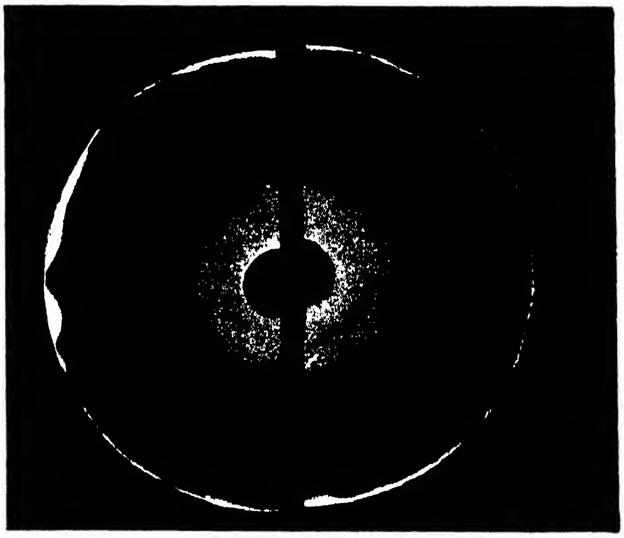


FIG. 1. X-ray diagram of asphaltenes in asphaltic bitumen, showing presence of graphitic carbon (Debye-Scherrer method).

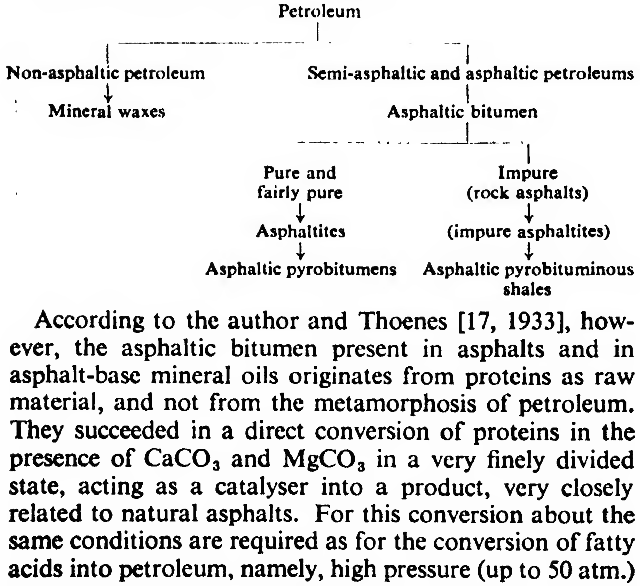
Besides elementary carbon many other products may play the role of micelle kernels in these systems, such as fine mineral powders or fillers. Principally these systems may be built up from an oily medium, lyophile protective bodies, and lyophobe micelle kernels; but there is no special requirement as to the nature of the kernels.

In coal tars the micelle kernels consist of elementary carbon for the greater part of graphitic character.

A second important problem is that of the *genesis of asphaltic bitumen and asphalt*. In the opinion of many investigators, e.g. H. Abraham in his well-known work *Asphalts and Allied Substances* [1, 1929], petroleum when once formed is gradually converted into the other types of asphaltic bitumen or pyrobitumen, under the influence of time, heat, and pressure. This process of transformation is known as metamorphosis. According to a theory, advanced by Richardson, mineral matter in a finely divided form, as, for example, colloidal clay, hastens the transformation of natural gas or petroleum by acting as a catalyser. In studying the well-known Trinidad asphalt lake deposit, Richardson concludes that an asphaltic petroleum existing at a considerable depth is converted into a more solid form of bitumen upon being thoroughly emulsified with colloidal clay, sand, and water through the medium of natural gas at a high pressure. During the metamorphosis hydrogen is gradually eliminated, the hydrocarbons becoming enriched in carbon, and from a chemical standpoint more complex structurally. The changes brought about during this process may be regarded as a form of *polymerization*, in which the hydrocarbon molecules become rearranged into more complex molecules of higher molecular weights. Abraham summarizes his views as follows:

From this view-point we may regard petroleum as passing in gradual stages under the influence of time, heat, pressure, and catalysers into the soft native asphalts, which in turn pass into harder native asphalts and then into asphaltites, and finally into the asphaltic pyrobitumens and asphaltic pyrobituminous shales [1, 1929]. In the American nomenclature asphaltic bitumen and asphalt are called asphalt.

Abraham gives the following scheme:



According to the author and Thoenes [17, 1933], however, the asphaltic bitumen present in asphalts and in asphalt-base mineral oils originates from proteins as raw material, and not from the metamorphosis of petroleum. They succeeded in a direct conversion of proteins in the presence of $CaCO_3$ and $MgCO_3$ in a very finely divided state, acting as a catalyser into a product, very closely related to natural asphalts. For this conversion about the same conditions are required as for the conversion of fatty acids into petroleum, namely, high pressure (up to 50 atm.) and a temperature of about 300°. Generally the raw material for this conversion consists of a mixture of proteins and fats or fatty acids, and so it depends upon the proportion of both components, which products may be formed under the influence of high pressure and temperature.

From this view-point the formation of the micelle kernels depends chiefly upon the protein content of the raw material for the asphaltic bitumen and mineral oil, while the fats and fatty acids of that raw material are transformed in mineral oil or into the oily medium of asphaltic bitumen. The following scheme illustrates these views:

Raw material	Product
Fats or fatty acids with very small protein content.	Mineral oil with low asphaltene content (Paraffine base oils or non-paraffinic).
Fats or fatty acids with medium protein content.	Asphalt base oils.
Fats or fatty acids with high protein content.	Asphaltic bitumen.
Fats or fatty acids with high protein and $CaCO_3$ content.	Asphalt.

A third important problem is that of the *conversion of mineral oils into asphaltic bitumen*. This problem is closely related to the first mentioned: the nature of the micelle kernels. The transformation of the hydrocarbons present in mineral oils into the micelle kernels of asphaltic bitumen may be characterized as a *dehydrogenation*. The older views (polymerization (Engler [3, 1913]) and formation of oxygen or sulphur-containing compounds (Marcusson [6, 1931])) are definitely to be discarded. There are no indications that polymerization plays an important part in the formation and transformation of asphaltic bitumen. Regarding Marcusson's hypothesis, it may be noted that when oxidizing mineral oils with air (blowing process), analysis shows that little or no oxygen actually combines with the hydrocarbons.

The principal reagents for the conversion of hydrocarbons into asphaltic bitumen are *oxygen* and *sulphur*. Abraham [2, 1929] gives the following scheme for the dehydrogenation:

$$C_xH_y+O\rightarrow C_xH_{y-2}+H_2O$$
$$C_xH_y+S\rightarrow C_xH_{y-2}+H_2S.$$

He supposes a gradual dehydrogenation. This must lead to the formation of micelle kernels, consisting of big molecules of high carbon content.

The author's scheme [14, 1932] for the dehydrogenation is quite different. He supposes the presence of mono-atomic carbon radicals in mineral oils, which are converted into elementary carbon, the micelle kernel of asphaltic bitumen in the following way:

$$\begin{array}{l}CH\\ CH_2+O_2\rightarrow C+CO+CO_2+H_2O\\ CH_3\end{array}$$

$$\begin{array}{l}CH\\ CH_2+S\rightarrow C+H_2S\\ CH_3\end{array}$$

The hypothesis of the presence of active radicals in mixtures of hydrocarbons originates from Bone, who made the supposition that in pyrogenic reactions mono-atomic carbon groups such as CH_3, CH_2, and CH having a real, but fugitive, existence play an important part. The author modified and extended this hypothesis in this way—that these mono-atomic carbon radicals are supposed to exist permanently in mineral oils as dissociation products. It is not easy to get a direct proof for the existence of these dissociation products, but all these dehydrogenation reactions may be readily explained as reactions between these groups and the dehydrogenating reagent.

Many problems remain in this field: here colloid chemistry has to wait until organic chemistry has brought more light in the apparently very complicated problem of the composition of these hydrocarbon mixtures.

REFERENCES

1. **Abraham, Herbert.** *Asphalts and Allied Substances*, 3rd ed. 61. New York, 1929.
2. —— *Asphalts and Allied Substances*, 3rd ed., 44 and 47.
3. **Engler-Höfer.** *Das Erdöl u. s. Verwandte*, **1**, 671 (1913).
4. *J.S.C.I.* **24**, 310 (1905).
5. **Lord**, E. C. E. *J. Agric. Research*, **17**, 167 (1919).
6. **Marcusson**, J. *Die natürlichen und künstlichen Asphalte*, 15 (1931).
7. **Nellensteyn**, F. J. *Chem. Weekbl.* **22**, 291 (1925).
8. —— *Chem. Weekblad.* **22**, 565 (1925).
9. —— *J.I.P.T.* **14**, 134 (1928).
10. —— *Proc. World Petr. Cong.* **2**, 577 (1933).
11. —— *Proc. World Petr. Cong.* **2**, 618 (1933).
12. **Nellensteyn**, F. J., and **Loman**, R. *Asfaltbitumen en Teer.* Amsterdam, 1932.
13. —— —— *Asfaltbitumen en Teer*, 31. Amsterdam, 1932.
14. —— —— *Asfaltbitumen en Teer*, 19. Amsterdam, 1932.
15. **Nellensteyn**, F. J., and **Roodenburg**, N. M. *Chem. Ztg.* **85**, 819 (1930).
16. —— —— *Kolloid Chem.* Beihefte **31**, 434 (1930).
17. **Nellensteyn**, F. J., and **Thoenes**, D. *Chem. Weckblad.* 30, 359 (1933).
18. **Richardson**, Cl. *Modern Asphalt Pavement.* New York, 1905. *Proc. A.S.T.M.* **6**, 509 (1906); *J. Phys. Chem.* **19**, 241 (1915); *Ind. Eng. Chem.* **7**, 463 (1915); **8**, 4 (1916).

SULPHURIC ACID SLUDGES AND SULPHURIC ACID RECOVERY

By T. C. OLIVER, B.S., E.M., and S. F. SPANGLER, B.S., Ch.E.
Vice-Presidents, Chemical Construction Corporation, New York

1. Introduction; Nature of Petroleum Acid Sludges; Problems of Sulphuric Acid Recovery; Early Methods of Recovery

Introduction. The treatment of petroleum distillates with sulphuric acid results in the formation of reaction products which remain associated with the unconsumed acid as a viscous liquid or semi-solid material, known variously as petroleum acid sludge, refinery acid sludge, sulphuric acid sludge, or acid sludge. The utilization of this material is a problem as old as the petroleum-refining industry itself. The value of the sulphuric acid used only in treating lubricating oils in the United States in 1929 has been estimated at $8,300,000.00, of which 40% was irrevocably lost [56, 1930]. These figures are exclusive of the acid used in treating other petroleum products such as gasoline. While the general business depression and the development of other refining methods has somewhat reduced the consumption of sulphuric acid in recent years, the total quantities used are still impressive, being reliably estimated as exceeding 680,000 tons, computed as equivalent sulphuric acid monohydrate, for 1934 in the United States alone [1, 1935]. Unfortunately the fact that the petroleum technologist is ordinarily highly trained in organic chemistry, while sulphuric acid is an inorganic compound, has resulted in the refinery acid plant receiving 'step-child' treatment in many cases and not the careful study merited by its economic importance.

Nature of Petroleum Acid Sludges. The composition of acid sludge is exceedingly complex and varies considerably with the nature of the oil treated as well as with the strength of acid and the treating technique used. Nevertheless, since the different types of petroleum differ from each other only in containing different proportions of common basic constituents, the composition of acid sludges can be predicted from a study of the reactions between sulphuric acid and these basic constituents of petroleum. These reactions may be summarized for the principal constituents as follows:

(*a*) *Paraffins.* Pure paraffins give practically no reaction with sulphuric acid, but in mixtures with naphthenes they may be dissolved, oxidized, and sulphonated [14, 1923; 53, 1930].

(*b*) *Naphthenes.* Pure naphthenes give practically no reaction with sulphuric acid, but in mixtures with paraffins and other hydrocarbons they may be dissolved, oxidized, and sulphonated, especially if the treatment is carried out at high temperatures and with concentrated or fuming sulphuric acid [9, 1930; 14, 1923; 53, 1930].

(*c*) *Aromatic Hydrocarbons.* Aromatic hydrocarbons react with sulphuric acid to form sulphonic acids which are partly dissolved in the acid sludge. Some are dissolved without the formation of sulphonic acids, while others may form condensation products with olefines and other hydrocarbons under the influence of sulphuric acid [43, 1927; 53, 1930].

(*d*) *Unsaturated Hydrocarbons.* One of 'he chief objects of the acid treatment of oils is the removal of certain unsaturated hydrocarbons, especially those which tend to form gums or to discolour the product. Several possible reactions may occur, including (1) polymerization, (2) formation of mono- and di-alkyl-sulphuric esters, (3) formation of secondary and tertiary alcohols, (4) formation of condensation products with aromatic hydrocarbons, and (5) oxidation. Some of the polymers remain in the sludge, dissolved in sulphuric acid, while others remain in the treated oil. As the amount of polymerization increases with high treating temperatures and high acid strengths, low-temperature treatment has been suggested to reduce polymerization losses [8, 1928; 16; 43, 1927; 44, 1927]. Some of the unsaturated hydrocarbons combine with the sulphuric acid to form esters which are partially dissolved in the acid sludge. Subsequent treatment of the sludge with water will result in the formation of alcohols from these esters. If the original treatment of the oil is made with acid of less than 100% strength, in other words, if water is present originally, the esters may be partially decomposed into secondary and tertiary alcohols immediately [7, 1926]. Some unsaturated hydrocarbons such as olefines also combine with aromatic hydrocarbons to form condensation products which probably remain dissolved in the acid sludge to a considerable degree. Sulphuric acid also has a strong oxidizing effect on many unsaturated hydrocarbons, producing alcohols, aldehydes, and ketones with attendant formation of sulphur dioxide which largely remains dissolved in the acid sludge. The amount of oxidation is influenced by the presence of any substances which may act catalytically such as metals, alkali salts of naphthenic acids, sulphur compounds, and tarry and asphaltic oxidation products, and is usually accompanied by polymerization and condensation [9, 1930; 53, 1930; 54, 1931].

(*e*) *Oxygen Compounds.* Oxygen-containing compounds such as naphthene acids, phenols, &c., are usually dissolved in the acid sludge, with or without an attendant reaction [55].

(*f*) *Nitrogen Compounds.* Nitrogen compounds such as pyridine, quinolines, and their hydro derivatives usually combine with the sulphuric acid to form salts that are removed in the acid sludge [55, 1931].

(*g*) *Sulphur Compounds.* Another primary object of acid treatment is the removal of sulphur compounds which would otherwise form corrosive compounds in the final product. In addition to traces of free sulphur, petroleum has been found to contain varying quantities of hydrogen sulphide, mercaptans, sulphides, thiophenes, thionaphthenes, sulphoxides, sulphones, and sulphonic acids. These sulphur compounds are mostly physically dissolved in the acid sludge, but oxidation and sulphonation may also occur [3, 1928; 4, 1929].

(*h*) *Asphaltic and Resinous Compounds.* While the complete removal of these substances is one of the major purposes of acid treatment, very little is known about the exact chemical reactions that take place between asphaltic and resinous compounds and sulphuric acid. In general, oxidation, sulphonation, and polymerization probably occur with solution of the product in the acid sludge.

Since acid sludge can have a very complex and variable chemical composition, it follows that its physical properties also vary widely. Three different types can be broadly distinguished:

1. (1) Liquid sludge from gasoline and kerosine refining. This type usually keeps liquid at all times and contains 40–60% free sulphuric acid (as determined by titration).
2. (2) Light lubricating-oil sludge. This is a black, pitchy, viscous fluid which oxidizes and solidifies, containing, e.g., 44% sulphuric acid, 8% sulphonic acid, and 18% pitch.
3. (3) Heavy lubricating-oil and paraffin sludge. This is an extremely heavy, pitchy mass which solidifies rapidly when cool and must be handled hot, and contains about 25–30% sulphuric acid.

Problems of Sulphuric Acid Recovery. Prior to the increased use of petroleum products, following the World War, and the attendant growth in quantities of acid sludge produced, the problem of sulphuric acid recovery received slight attention except at the largest refineries. The smaller refineries, producing relatively little acid sludge, merely attempted to dispose of the sludge where it would do the least harm. Frequently raw acid sludge was allowed to form large ponds on waste land adjacent to the refinery, where it resulted in gradual contamination of the ground by the acid and damage to nearby vegetation. At refineries on the sea coast acid sludge was frequently discharged into the ocean, directly or by barges which dumped their contents a few miles off the coast. Some refineries followed the practice of burning their acid sludge, occasionally in open fields, but usually under boilers. With sludges of high acid content this practice required admixture with other fuels. Aside from the fact that burning of the sludge represents an entire loss of the valuable acid content and a relatively inefficient use of the fuel content, the resultant combustion gases contain large quantities of sulphur dioxide and some sulphur trioxide, which cause objectionable atmospheric pollution. Also there is a risk of serious corrosion of boilers and stacks unless the gases are always kept sufficiently hot to prevent any condensation of moisture. At some places the acid in the sludge is neutralized by mixing with alkalies or alkaline sludges before the sludge is burned; this procedure eliminates the objectionable acid content from the combustion gases, but involves additional expense while saving nothing except the fuel value of the sludge. Accordingly, combustion of sludge has been generally abandoned at modern refineries in favour of some system of recovering the acid content [36, 1933].

Early Methods of Acid Recovery. Until comparatively recently all commercial methods for the recovery of sulphuric acid from refinery acid sludge have been based on a separation of the sludge into weak acid, called separated sludge acid, and hydrocarbons known as acid oils and acid tars. The separation is accomplished by diluting the acid sludge with water, followed usually by heating with steam, after which the acid and hydrocarbons separate in layers. Sludges formerly available were readily separated by this procedure, which was ordinarily conducted in open lead-lined steel tanks, preferably provided with conical or inclined bottoms and outlets at various elevations.

The separated sludge acid was ordinarily produced at a strength of 35–45% H_2SO_4, with a brown-black colour due to the presence of hydrocarbons. This acid was then concentrated in open lead pans heated with steam coils and glass or cast-iron externally fired retorts to a strength of nearly 66° Bé. (90–3% H_2SO_4), which was suitable for reuse in treating. This method of concentration involved high maintenance expense for equipment and was attended with heavy acid losses from decomposition of the sulphuric acid into sulphur dioxide through oxidation of the organic matter at the necessary high temperatures employed when producing strong acid. The increased use of sulphuric acid in refineries following the World War, combined with a change in the character of the acid sludge which resulted in the production of separated acids containing higher quantities of hydrocarbons, led to the abandonment of this old method of acid concentration in favour of methods not involving such heavy losses and expense.

2. Recovery of Weak Sulphuric Acid by Separation of Sludge; Open Tank Separation; Pressure Separation; Pressure Digestion of Partially Separated Acid

Recovery of Weak Sulphuric Acid by Separation of Sludge. As stated in the previous section, separation of sludge into weak sulphuric acid and hydrocarbons is the first step in the conventional method of acid recovery. Ordinarily this separation is a fairly easy process, especially in the case of sludges from paraffin-base oils. However, sludges derived from asphaltic- or naphthenic-base oils are more difficult to separate due to their content of sulphonic and naphthenic acids, which will not separate out at ordinary boiling temperatures and must be heated under pressure. Some sludges, for example those produced in the treatment of medicinal oils with fuming sulphuric acid, can scarcely be separated by any commercially feasible method and their acid content can only be recovered by other more recently developed processes. While other processes of separation involving, for example, diffusion through porous membranes, or addition of chemicals as coagulants or as solvents, have been suggested and are disclosed in many patents [37, 1933], only those processes which involve dilution with water, with or without additional heating, have become of commercial importance due to either the expense or inefficiency of the other processes. These commercial processes can be conveniently classified as open tank separation and as pressure separation.

Open Tank Separation. In the case of the readily separable sludges the operation is usually conducted in open lead-lined tanks. The operation is conducted intermittently as a batch process. A charge of sludge is run into the tanks, diluted with water, and agitated with air, steam, or mechanically. Where the heat of dilution is not sufficient, additional heat is supplied from either open or closed steam coils. Experiments are necessary to determine the proper dilution and temperatures for each type of acid sludge. While it is desirable to produce as strong a separated acid as possible in order to minimize the subsequent expense of evaporating water in the concentrators, too strong a separated acid carries with it larger quantities of hydrocarbons which increase decomposition losses in the subsequent concentration. Ordinarily, open tank separation is conducted to give an acid containing 35–45% H_2SO_4.

In open tank separation three layers of material are generally produced. The top layer contains polymerized and partially sulphonated oil, known as acid oil, the middle layer or acid tar is of a viscous or cokey character and contains some sulphonated products, while the separated sludge acid constitutes the bottom layer. Some types of sludge give only two layers, the upper consisting of the oily substances and the lower of diluted acid.

The fumes from open tank separation are in many cases very obnoxious. Some sulphur dioxide is always liberated, but frequently the gases also contain combustible hydrocarbons. At some refineries covered tanks are used provided with an outlet connected to a fume furnace in which the odoriferous gases are burned. As the gases do not ordinarily contain enough hydrocarbons to support combustion themselves, some form of cheap fuel must also be used if this procedure is followed.

The acid oil and acid tar recovered in the separation are usually burned as refinery fuel, with or without washing to remove residual acid. These materials are relatively rich in sulphur compounds and have a strong odour, hence little attempt is made to sell them for outside use.

Pressure Separation. Acid sludges which cannot be satisfactorily separated at ordinary boiling temperatures can frequently be handled in a pressure separator. This is essentially a high-pressure autoclave, usually of horizontal cylindrical form with hemispherical ends, heavily lined with lead and acid-resistant masonry. The sludge is introduced into the autoclave, then diluted with water and heat applied internally by live steam to give a temperature of 325–350° F. The operation may be run intermittently in batches, though it is usually considered preferable to withdraw the acid oil nearly as fast as it separates out in order to prevent coking during prolonged heating. Considerable skill is required in designing and erecting this type of separator, and its commercial exploitation has been largely confined to the equipment jointly controlled by the Standard Oil Company of California and the Chemical Construction Corporation under a group of patents [13, 1924; 18, 1926; 19, 1930; 33, 1926; 34, 1926].

The weak acid produced in a pressure separator is usually slightly stronger than that produced in open tank separation, having a strength of 40–50% H_2SO_4. The reduced cost of concentrating this stronger acid partially offsets the higher costs of pressure separation.

As the pressure separator is a closed vessel, it is comparatively easy to vent it through a relief valve to a fume furnace so that obnoxious odours are avoided. From the nuisance elimination standpoint the pressure separator has, therefore, decided advantages over the open tank separator. The maintenance expense is unfortunately heavier, but this is compensated for by the ability of this equipment to handle otherwise unseparable sludges.

Pressure Digestion of Partially Separated Acid. It has been found that certain acid sludges, which are more readily separated in open tanks than in a pressure separation, give a separated acid which contains somewhat more hydrocarbons than is desirable for satisfactory further concentration of the acid. The Chemical Construction Corporation offer a modified form of their pressure separator in which this partially separated acid is further heated under several atmospheres pressure, with resultant separation of the residual hydrocarbon content and production of a cleaner and more concentrated separated acid. The gases from the pressure digestor are customarily passed through a fume furnace before their release to the atmosphere.

3. Concentration of Weak Separated Acid; Disadvantages of Early Methods; Concentration under Vacuum; Concentration with Hot Flue Gases; Fortification of Concentrated Acid; Disadvantages of Present Methods

Concentration of Weak Separated Acid. Since the greater part of the sulphuric acid used in treating petroleum products is at a strength of 66° Bé. (theoretically 93% H_2SO_4) or higher, the weak acid produced in any separation process cannot be considered as a completely recovered product. Formerly it was possible to use some of this weak separated sludge acid for the manufacture of superphosphate fertilizer, but the objections of governmental fertilizer control departments, as well as of the users, to the presence of evil-smelling hydrocarbon derivatives in superphosphate has practically stopped this procedure. Furthermore, weak sulphuric acid can be neither readily nor economically transported any considerable distance, so concentration to a re-usable strength at the point of production is almost a necessity.

Before considering available methods of acid concentration, the meaning of the term '66° Bé.', as applied to sulphuric acid, requires clarification. Specific gravity can be used as an accurate measure of the strength of sulphuric acid only up to a strength of 93·19% H_2SO_4. Above this point the specific gravity at first decreases slightly and then rises with increasing strength, so that a chemical analysis, usually by titration with alkali, is necessary to determine the true strength of the acid. Pure sulphuric acid containing 93·19% H_2SO_4 has a specific gravity of 1·8354, corresponding to 66° Bé. on the standard American heavy Baumé scale. Concentrated sludge acid, however, contains coke, from the decomposition of the hydrocarbons, as well as hydrocarbon compounds, which give it a specific gravity higher than that for pure sulphuric acid of the same H_2SO_4 content. Consequently 66° Bé. sludge acid often contains as little as 88% H_2SO_4, at times even less, and rarely more than 92% H_2SO_4, depending on its carbon content. However, the impurities which reduce the acidity while maintaining the high specific gravity of concentrated sludge acid have apparently little detrimental effect on the treating power of the acid unless present in excessive quantities. Apparently the treating power is dependent on the analysis of the liquid portion of the sludge acid, considering the coke as an inert solid. Thus, for example, a concentrated sludge acid testing 66° Bé., but analysing 90% H_2SO_4, 3% carbon, and 7% water, will be practically as effective as one analysing 92% H_2SO_4, 0·84% carbon, and 7·16% water, since they both contain the same ratio of H_2SO_4 to water. This fact only has made it possible to employ concentration processes for the production of a satisfactory recovered acid from the impure separated acids produced in recent years.

It should also be noted that while pure sulphuric acid can be concentrated by evaporation to a strength of 98% H_2SO_4, this requires such high temperatures that acid losses by volatilization become excessive, and this procedure is rarely used commercially. It is entirely impracticable for sludge acid, as the losses from decomposition at these temperatures would be enormous. Consequently a strength corresponding to 66° Bé. is the maximum to which sludge acid is concentrated commercially, and when stronger acids, e.g. 98% H_2SO_4 or fuming 20% oleum, are required for treating, they can only be made from acid sludge by fortification of the concentrated (66° Bé.) acid or by the thermal decomposition method, which does not include separation and concentration.

Disadvantages of Early Methods. The demand during the World War for strong sulphuric acid for use in the manufacture of explosives led to the development of several types of concentrators highly satisfactory for the evaporation of clean sulphuric acid, i.e. acid not containing hydrocarbons, to a strength of 93%. In addition to numerous improvements to the old pan, retort and cascade concentrators using indirect heat, tower systems of concentration were developed by Gaillard, Gilchrist, and Kalbperry in which the acid was brought in direct contact with hot combustion gases. The growing demands of the oil industry following the War led to attempts to apply these systems to the concentration of separated sludge acid but with entirely unsatisfactory results [49, 1929]. Two principal difficulties were encountered.

The first lay in the tendency of the sludge acid to foam at a certain stage of concentration, owing to the decomposition of the acid by the hydrocarbons present even in the relatively clean separated acids then common. This difficulty was first successfully overcome in 1920 by the use of the two-stage submerged-pipe concentrator, described hereafter in more detail under concentration with hot flue gases. The foaming was found to occur when weak feed acid was introduced into hot partially concentrated acid of a certain strength, depending upon the exact character of the sludge acid but usually in the neighbourhood of 55° Bé. This strength was found to be that at which coke begins to form as the acid is concentrated. The two-stage process surmounted this difficulty by conducting the concentration in two steps in two separate continuously operated evaporators. In the first unit the weak acid is concentrated to a strength just under the coking point, and this intermediate strength acid is then concentrated in the second unit to its final strength of 66° Bé. The continuous two-stage process was employed in the many installations made by the Chemical Construction Corporation under basic patents granted to Hechenbleikner and Oliver [27-31, 1922; 32, 1923].

The second difficulty arose from the excessive decomposition of the sulphuric acid by oxidation of the hydrocarbons and coke at the high temperatures (529° F.) necessary to produce 66° Bé. acid by direct evaporation. The obvious solution of this is to attempt to reduce the necessary temperature by conducting the evaporation under reduced pressure. In the Chemico (Hechenbleikner-Oliver) continuous two-stage process this is accomplished by blowing the hot combustion gases through the acid bath so as to reduce the vapour-pressure and give the effect of a partial vacuum [20, 1918; 42, 1916]. Other widely used commercial concentrators employ a high vacuum in the evaporator, with indirect heating.

Concentration under Vacuum. While several forms of sulphuric acid concentrators operating under high vacuum are available, the Simonson-Mantius Vacuum Concentrator [38, 1933; 39, 1928; 47, 1921] has found the widest acceptance in the oil industry.

In the original form of this equipment a water jet or evactor was used capable of giving a vacuum of 28 in. mercury. The concentration of sulphuric acid to 61° Bé. only requires this degree of vacuum as the boiling-point then does not exceed 260° F. and a steam pressure of 45 lb. will give a minimum temperature difference of 30° F. With a steam pressure of 100 lb., the acid can be concentrated to about 63° Bé., but in order to reach 66° Bé. under 28 in. vacuum, it is necessary to use hot oil at 500° F. as a heating medium. As a still higher vacuum would produce a corresponding decrease in the boiling-point of the acid and permit the use of steam instead of hot oil for producing 66° Bé. acid, recent forms of the Simonson-Mantius concentrator are supplied with multi-jet steam evactors capable of producing a vacuum of 29·8 in. With this vacuum, 66° Bé. acid can be produced with 100 lb. pressure steam and 65° Bé. acid with 45 lb. pressure steam.

The shell or housing of the Simonson-Mantius concentrator is built of cast iron or steel in suitable sections, and heavily lined with chemical sheet lead and acid-proof masonry. In concentrators producing up to 61° Bé. acid, the heating element consists of coils of lead pipe. For concentration to 66° Bé. special high silicon iron tubes are used for the heating surface. All concentrators are equipped with entrainment separators, in addition to the condensers specially designed to handle hot acid and water vapours. Where oil is used as the heat transfer medium, it is heated in a separate oil furnace especially adapted for use with this type of concentrator.

Over 60 Simonson-Mantius concentrators of various types have been installed at oil refineries throughout the world. Either batch or continuous concentration is employed, depending on conditions and type of acid. This type of concentrator has the advantage of eliminating all fume nuisance, since any waste gases are carried away in the condensed vapours discharged from the evactor. It has the disadvantage, inherent in all concentrating equipment, that the strength of the product acid is limited by the impurities present which will decompose the acid into sulphur dioxide gas if the heating is carried too high. Any sulphur dioxide so formed is, of course, a total loss as it is carried away in the discharged condensate. Owing to its fume elimination feature the Simonson-Mantius concentrator has proved especially useful in congested industrial districts.

Another form of vacuum concentrator, employing a series of steam-jacketed high silicon iron tubes, is offered under the name of Flash-film Concentrator by the Chemical Construction Corporation of New York [25, 1934]. This unit also uses a water-jet evactor for the production of the high vacuum and has the advantage that its capacity can be increased by adding additional tubes after the original installation has been made.

Concentration with Hot Flue Gases. The leading commercial process employing hot flue gases is the Chemico two-stage submerged-pipe system previously mentioned in connexion with the Hechenbleikner-Oliver patents. As originally installed, this system consisted of two independent units, supplied with hot gases from a common oil or gas-fired furnace, operated under forced draft. Each unit consists of a covered acid-proof masonry pan communicating with an acid-proof masonry preheating tower. The combustion gases, with an excess of oxygen, are forced at a temperature of about 1,100° F. under the surface of the acid contained in the pan, rise through the acid, and pass into the tower where they preheat the descending supply of feed acid. In the first, or low-stage, unit the acid is concentrated from about 30° or 35° Bé. to between 50° and 55° Bé. and much of the hydrocarbon content is removed by either volatilization or oxidation. This 50–55° Bé. acid, after passage through an intermediate storage tank, when carbonaceous compounds may be either skimmed off or settled out, is fed to the second, or high-stage, unit where it is concentrated to 66° Bé. strength. The waste gases from both units are combined and passed through a Cottrell electrical precipitator, where any sulphuric acid mist is condensed as weak acid and returned to the concentrators.

In 1928 a modification of this concentrator was introduced under the name of the Chemico Drum-Type Concentrator, which is described in patents issued to Mast [41, 1931, 1934] and Hechenbleikner [26, 1935]. This newer arrangement involves a 'series' flow of gases as compared with a 'parallel' flow in the older type. In the Drum-Type Concentrator the exit gases from the second, or high, stage are passed into the first, or low, stage concentrating bath, though some of the hot furnace gases may also be introduced directly into the low stage when handling certain grades of acid. The expensive high preheating towers are omitted entirely. The concentrator consists essentially of a long, horizontal steel drum divided into three compartments. The front compartment is lined with insulating and fire brick, and equipped with an oil or gas burner operated under forced draft from a centrifugal air-blower. The other two compartments are lined with heavy sheet lead and acid-proof masonry. Hot gases from the combustion furnace at a temperature of around 1,100° F. are released under the surface of the acid in the middle or high-stage compartment. When 66° Bé. acid is being produced in the high stage, the gases leave this chamber at about 450° F., carrying with them a small quantity of acid mist, and are released beneath the surface of the acid in the rear or low-stage compartment. They emerge from this compartment at a temperature of 200–300° F., depending on the strength of the weak acid fed the low-stage compartment. These gases are then cleaned before being released to the atmosphere by passage through a Cottrell electrical precipitator or some equivalent absorption or scrubbing tower. The weak acid is fed continuously to the rear compartment by an air lift or pump. When handling sludge acid in this equipment it is preferable to pass the acid from the rear compartment into an intermediate storage tank through a skimmer where impurities can be removed, after which the acid is pumped by an air lift into the middle compartment, though, when sufficiently clean acid is being handled, direct gravity flow from the rear to the middle compartment through a luted passage is feasible. The strong finished acid is drawn off from the middle compartment through a cooler to storage. The violent agitation of the acid caused by the passage of the hot gases prevents settling out of residues inside the drums. The use of waste gases from the high stage as a source of heat for the low stage gives greater heat economy than was possible in the earlier tower system, where the gases from the high-stage unit were released through the precipitator.

Approximately 75 Chemico submerged-pipe concentrators of the two types previously described have been installed throughout the world for the concentration of separated sludge acid, in addition to numerous units operating on other grades of sulphuric acid. The Drum-type sludge acid concentrator installations vary in size from small units producing 5 tons of 66° Bé. acid daily to a battery of 5 large units producing a total of 175 tons of 66° Bé. acid daily.

When concentrating to a strength of 66° Bé. with hot gases, the exit gases from the concentrating unit proper contain too much sulphuric acid mist for direct release to the atmosphere. The early installations were provided with gas scrubbing towers, but since 1921 Cottrell electrical precipitators have been the standard equipment for the removal of this acid mist. These precipitators are of the pipe or tubular type, and employ rectified alternating current at a potential of 60,000 to 80,000 volts [40]. Formerly, lead was used exclusively for the construction of the precipitator pipes. Precipitators with high silicon iron pipes were introduced in 1928 to avoid risk of deformation of the pipes at elevated temperatures. Owing to the difficulty of producing perfectly straight and uniform pipes, this use of silicon iron has been largely abandoned, and moulded carbon tubes are used in modern precipitators operating at temperatures where lead is not considered desirable.

Fortification of Concentrated Acid. As previously explained, 66° Bé. is the upper limit of strength for economical concentration, and with separated sludge acid this gravity usually means several per cent. under 93% H_2SO_4. Modern sludge acids frequently contain so much carbon that they cannot be concentrated above 65° Bé. or above 85% H_2SO_4. Many treating processes require the use of 98% H_2SO_4 or 104½% H_2SO_4 (fuming acid or oleum with 20% SO_3). These higher-strength acids can only be produced directly by the contact or catalytic process of sulphuric acid manufacture, in which dry sulphur dioxide gas is oxidized in the presence of a catalyst to sulphur trioxide, which is absorbed in strong sulphuric acid. Concentrated sludge acid can be fortified or strengthened by mixing with the stronger acids produced by the contact process. Obviously the possible strength of the resultant mixture will depend on the quantities and strengths of the two acids mixed, and it would not be feasible for the refinery to add more fresh contact acid than the amount needed to replace the acid lost in treating, separating, and concentrating. On the average these losses total approximately one-third of the acid used in treating.

Gilchrist [17, 1930] has presented tables showing the strength of the concentrated acid necessary to produce various strengths of resultant acid when fortifying with new acid of various strengths, assuming that the new acid added must not equal more than one-third of the resultant total. These tables show that in order to produce a resultant acid containing 93% H_2SO_4, the concentrated sludge acid must contain 90·7% H_2SO_4 when fortifying with 98% acid, and 88·2% H_2SO_4 when fortifying with 104½% acid. To produce, under the same assumption, a resultant acid containing 98% H_2SO_4, the concentrated acid must contain 95·1% H_2SO_4 when fortifying with 104½% acid, and 93·3% H_2SO_4 when fortifying with 109% acid. Since neither 95·1% nor 93·3% H_2SO_4 can be made economically from separated sludge acid, it is commercially impractical to produce a 98% acid by fortification with purchased contact acid. Gilchrist shows, however, that high-strength acid can be made by fortifying concentrated sludge acid directly with sulphur trioxide.

Fortification with sulphur trioxide is possible at refineries possessing their own contact acid manufacturing plants, by using the concentrated sludge acid as the absorbent for the sulphur trioxide. By this method a resultant acid containing 93% H_2SO_4 can be produced from a concentrated acid of 83·0% strength and one containing 98% H_2SO_4 from a concentrated acid of 89·1% strength without adding more new acid (as sulphur trioxide) than the equivalent of one-third of the resultant total. This procedure has the additional advantage of reducing the cost of acid recovery as the cost of concentrating the sludge acid to these lower strengths, and the losses attending such concentration, are far less than when producing 66° Bé. acid.

As a result of the recent great simplifications in the contact process for manufacturing sulphuric acid commencing with the commercial use of vanadium catalyst in 1927 [49, 1929], numerous oil refineries have installed their own contact acid plants, thus becoming independent of outside sources of sulphuric acid supply. A description of contact acid manufacture can hardly be considered as within the province of an article reviewing sludge acid recovery, so the reader interested in pursuing this topic further is referred to the numerous standard works on this general subject and especially to the American Chemical Society Monograph on Sulphuric Acid by A. M. Fairlie, published in the Spring of 1936.

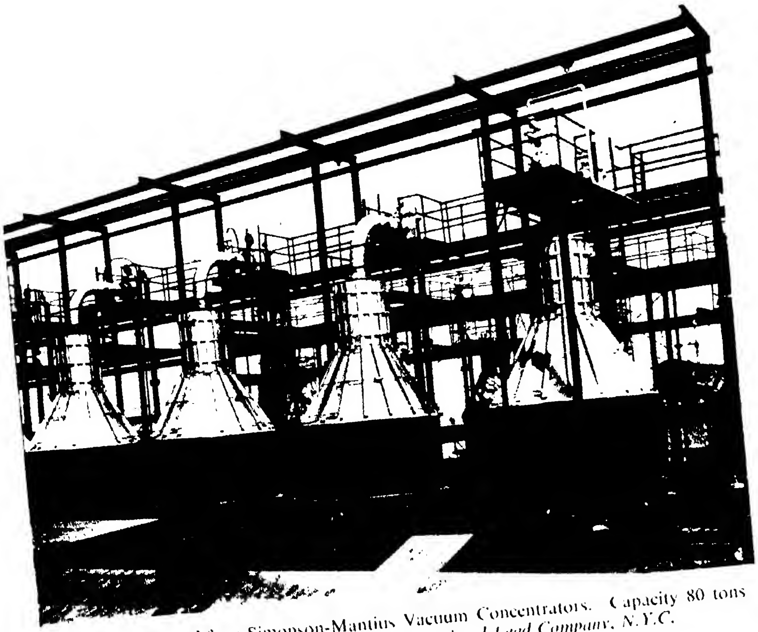


FIG. 1. Battery of four Simonson-Mantius Vacuum Concentrators. Capacity 80 tons 65° Bé. acid per day. *By the courtesy of National Lead Company, N.Y.C.*

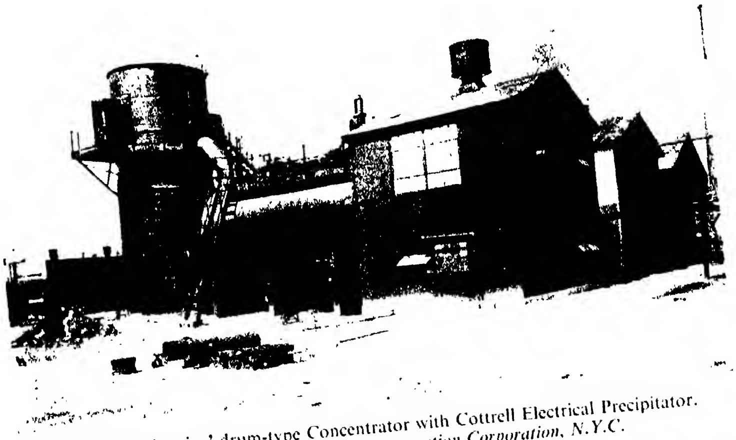


FIG. 2. 'Chemico' drum-type Concentrator with Cottrell Electrical Precipitator. *By the courtesy of Chemical Construction Corporation, N.Y.C.*

FIG. 3. Battery of 5 'Chemico' drum-type Concentrators. Capacity 175 tons 66° Bé. acid from 30° Bé. acid per day. *By the courtesy of Standard Oil Company of Indiana and Chemical Construction Corporation.*

Disadvantages of Present Methods. While some of the disadvantages of recovering sulphuric acid by the commonly accepted process of separating the sludge and concentrating the resultant weak acid have been overcome by the processes and equipment described in the foregoing pages, and especially by the adoption of fortification at refinery contact acid plants, the changes in the character of acid sludges resulting from changed methods of treating are rendering these processes obsolete. Except in isolated locations where sulphuric acid is unusually expensive, it is usually not economical to operate a contact acid plant producing less than 25 tons of sulphuric acid, computed as 100% H_2SO_4 equivalent, per day. Assuming that treating-separating-concentrating cycle involves a 33⅓% loss, this means that concentration by fortification with sulphur trioxide is economical only for refineries using at least 75 tons of acid daily. Refineries using less acid remain confronted with the increasing difficulty of producing a satisfactory strong recovered acid from increasingly contaminated sludges. When it is considered that some of the sludges now produced in the treatment of medicinal oils cannot be separated satisfactorily by any present method, the seriousness of this problem becomes more apparent. Its solution is discussed in the next subdivision of this article.

4. Recovery of Concentrated Sulphuric Acid from Sludge by Decomposition and Reforming

It has long been known that acid sludge, on standing, decomposes slowly into sulphur dioxide gas and a carbonaceous residue, and many inventors have proposed to accelerate this reaction by heat and use the sulphur dioxide for the production of sulphuric acid [2, 1923; 5, 1912; 6, 1911, 1916; 15, 1925; 35, 1930; 45, 1912, 1913; 46, 1910; 48, 1868; 51, 1889; 52, 1910]. These proposals varied considerably; some used external heat, others internal heat; some called for conducting the decomposition in stationary retorts, others in rotary furnaces; some operated as batch processes, others continuously. They were all distinguished, however, by one common feature—the failure to be successfully employed in a commercial plant.

The first successful commercial plant for the production of strong sulphuric acid by the decomposition of unseparated acid sludge was installed by the Chemical Construction Corporation in 1932 for the W. H. Daugherty & Sons Refining Company, at Petrolia, Pa. [50, 1933]. This plant employed a process developed by the late I. Hechenbleikner and his associates and previously tested on pilot plant scale.

In this process the decomposition of the sludge is produced by direct contact with a counter-current flow of hot combustion gases in a rotary kiln. These gases are produced from oil or gas and admitted into the rotary kiln at approximately 2,200° F. and with only a low oxygen content so as to prevent subsequent combustion of the hydrocarbon content of the sludge. The kiln is operated under a slight vacuum to eliminate loss of sulphur dioxide gas. Dry granular coke is discharged at the hot end of the kiln into a closed screw conveyor which removes it to a storage bin for subsequent use as a fuel. This residue is normally acid-free, high in volatiles and low in ash, and suitable for use as a pulverized fuel. Despite the high temperature of the combustion gases used, the material in the kiln is not overheated, and operations are conducted by controlling the rate of sludge feed, volume of air, and fuel used, so as to discharge the coke residue at a temperature of about 500–550° F. and the gases at 250–300° F.

The sludge is pumped into the kiln at the gas-exit end. If several different grades of sludge are to be handled, it is preferable to mix them thoroughly to secure a uniform feed to the decomposer. The gases leaving the decomposer contain around 20% of sulphur dioxide by volume, together with small quantities of condensable and uncondensable hydrocarbons, whose nature depends upon the original composition of the sludge, and considerable water vapour. These gases are passed through a series of washers for the condensation and removal of oils and moisture, and thence through a secondary combustion furnace where the uncondensable hydrocarbons are burned out. The gases next pass through a cooler and a Cottrell electrical precipitator (for removal of small traces of sulphuric acid mist formed in the secondary furnace) and enter a drying tower, where the last traces of moisture are removed by scrubbing with strong sulphuric acid. Air is admitted at this point to produce the proper ratio of sulphur dioxide and oxygen, and these mixed gases are then converted into sulphuric acid in a standard form of Chemico contact acid plant employing vanadium catalyst. The finished acid is produced at the same high strengths as are customary in contact acid plant operation, viz. 98% H_2SO_4 and 104½% H_2SO_4, and is of high purity, free of contamination by hydrocarbon compounds.

Since only the heat content of the combustion gases is utilized in the decomposition of the sludge and the nature of the gases is otherwise immaterial as long as they contain little free oxygen, it is possible by burning sulphur or waste hydrogen sulphide gas (recovered from still gases) as fuel instead of oil or gas to produce additional sulphur dioxide which will be converted into fresh, strong acid along with the sulphur dioxide produced from the sludge. Thus by making the contact acid-manufacturing section of the plant slightly larger than is necessary to handle only the sulphur dioxide producible from the acid sludge, it is possible to make in one plant, with one set of operators, at no additional cost beyond that of the sulphur or hydrogen sulphide used, the acid required for replacing cyclic losses as well as to recover the acid content of the sludge. A recovery of about 90% of the acid content of the sludge may be expected normally with this process. Since this recovery of acid is considerably greater than is obtainable by the usual separation and concentration method, the amount of new acid to be produced from sulphur is considerably less than is required with the usual acid recovery process. As the costs of recovering acid by this method have been shown by operation of the Petrolia installation to be less than those of the separation and concentration process, these two factors together give a considerable reduction in the net average cost of acid used in treating where this new process is employed.

The basic reaction of this Chemico-Hechenbleikner sludge conversion process is a reduction of the sulphate content of the sludge by the hydrogen atoms of the hydrocarbon. Apparently the carbon atoms of the hydrocarbons take no part in the reaction as there is normally no appreciable formation of carbon dioxide in the kiln and the original carbon content can be accounted for in the coke. The reaction, however, is controlled so as to stop with the formation of sulphur dioxide and avoid any production of elemental sulphur or hydrogen sulphide. More information as to details of the process and equipment may be obtained by a study of the group of patents held by the Chemical Construction Corporation [10–11, 1931; 21, 1933; 22–4, 1934].

An indication of the trend of recent development of the sludge decomposition is given by a French patent recently issued to the owners of the Hechenbleikner process [12, 1933]. While the process described in this patent has not been installed as yet in commercial plants, the authors of this article are in a position to state that it has been exhaustively tested on a semi-commercial scale and proved satisfactory with all types of refinery acid sludges. The essential features of the process may best be described by quoting from the French patent mentioned:

'The main use for the SO_2 gases from the decomposition of acid sludge is to reoxidize them to SO_3 in order to produce sulphuric acid for the oil refinery. When used in the contact process or even in the chamber process the presence of hydrocarbons in any considerable amount is very injurious. Unfortunately the gas obtained from the Hechenbleikner kiln, besides water and condensable hydrocarbons, contains a considerable proportion of uncondensable hydrocarbons and also some of the condensable hydrocarbons tend to form an oil mist which cannot be completely removed in the ordinary condensers. It became necessary to remove hydrocarbons in the Hechenbleikner process, and this was effected practically by burning them out. This method, while satisfactorily removing the hydrocarbons which would have otherwise been transformed into water in the contact plant with concomitant formation of the acid mist, diluted the gases very materially. In the sludges which are low in oil the amount of hydrocarbons was not sufficiently great, so that excessive dilution resulted from burning them out. On sludges of this type, therefore, the straight Hechenbleikner process operates with excellent commercial efficiency. When, however, high oil sludges are to be treated it became necessary to remove a part of the oil which was achieved by distilling off the more volatile hydrocarbons at low temperature, which left a sludge having the characteristics of low oil sludges and which could be satisfactorily handled in a straight Hechenbleikner process.

'We have found that the difficulties involved in the decomposition are completely obviated when, instead of using combustion gases as a heating medium, solids are used. These solids may be particles of fairly large size, such as iron balls, pebbles, and the like, or they may be finely divided solids, such as sand or coke. The solids are heated to a high temperature and are then contacted with an acid sludge in a closed vessel such as a kiln. Decomposition takes place extremely rapidly permitting great capacity from small apparatus and producing a very strong gas which may contain as high as 75% to 90% SO_2.

'The carbonaceous residue from the decomposition in the acid sludge is discharged with the spent heating bodies from the kiln, and is treated in one of two ways depending on the particle size of the heating medium used. Where the heating medium consists of large particles, such as metal balls, pebbles, or the like, the carbonaceous residue is preferably removed by a screen, and the balls or pebbles heated in a suitable heating kiln to bring them back to the initial temperature. Where the heating medium is in a finely divided state, such as hot sand or hot coke, a more efficient method may be used. No attempt is made to separate the carbonaceous residue from the heating medium, and on the contrary it is burned in contact with the heating medium, thereby serving as fuel and permitting the use of very simple apparatus, because, due to the fact that carbonaceous residue is in intimate contact with the heating medium, a very effective heat transfer is possible.

'Where the heating medium is hot coke instead of hot sand it may obviously be a portion of the carbonaceous residue produced. This has some advantages where a large amount of carbonaceous residue is obtained considerably in excess of that required to furnish sufficient fuel for the heating step. Since with hot coke the material discharged from the kiln is homogeneous, a portion of it may be removed and sold as fuel, part of the remainder being burned to heat the unburned carbon to the requisite temperature. The gas which is evolved, when cooled to condense out water and condensable hydrocarbons, has so low a hydrocarbon content as compared to SO_2 that the hydrocarbons can be burned out without any dilution problem, and in some cases it is not necessary to remove them at all, as where the hydrogen content is sufficiently low, so that after mixing enough air to bring the SO_2 to the proper concentration for use in the contact process, the hydrogen content is not more than 3 milligrams per cubic foot. While this complete elimination of hydrocarbon removal is only possible with certain sludges, in every case the removal of hydrocarbons is simplified and the bad results from excessive dilution are not experienced.'

Considering the results obtained with the commercial sludge decomposition plant at Petrolia, and especially the fact that during the last year it has regularly operated above its rated capacity whenever adequate quantities of acid sludge have been available, it may at first glance appear surprising that this acid-recovery system has not been more widely adopted. It must be borne in mind, however, that the quantity of sulphuric acid used in the oil industry has decreased in recent years, both from the general industrial depression and from the adoption of other methods of treating certain classes of oils. The effect has been to make it possible for many existing acid-recovery plants of the older type to meet the present requirements of their owners, even though the plants are in such a condition that they could not now be operated at their original designed capacity. Furthermore, the leading refineries, who would normally be the leaders in adopting a new process, are largely equipped with the latest types of separating and concentrating plants whose complete abandonment cannot as yet be economically justified. Since adoption of the sludge decomposition process necessarily involves installation of a contact acid manufacturing plant, the figure of 25 tons H_2SO_4 per day as the minimum economic capacity is again applicable and the majority of refineries requiring that quantity of acid is included in the group possessing unamortized recovery plants of the older type. In considering the question of minimum economic capacity, it should be noted, however, that with the sludge decomposition process, the figure of 25 tons H_2SO_4 per day refers to the total acid required by the refinery, while it referred only to the make-up or fortifying acid requirement when considering the installation of a contact acid plant in connexion with a separation-concentration system. It is the considered opinion of the authors of this article that the sludge decomposition method involving the production of strong fresh acid from unseparated sludge offers the most economical solution of the refinery acid problem and will be adopted in future new construction. This conclusion has been reached in spite of the fact that the company with which they are connected also offers equipment and processes employing the conventional older methods.

REFERENCES

1. Anon. *Chem. Met. Eng.* **42,** 44–6 (1935).
2. Bezanson, O. U.S.P. 1,459,084 (1923).
3. Birch, S. F., and Norris, W. S. *Trans. Fuel Conference, World Power Conference, London,* 1928, **1,** 641–68.
4. —— *Ind. Eng. Chem.* **21,** 1087–90 (1929).
5. Black, J. G., and Chappell, M. L. U.S.P. 1,031,413 (1912).
6. Blowski, J. S., and Blowski, B. A. U.S.P. 1,010,221 (1911) and 1,186,373 (1916).
7. Brame, J. S. S. *J.I.P.T.* **12,** 48–67 (1926).
8. Brooks, B. T. *J.I.P.T.* **14,** 738–55 (1928).
9. Catlin. *Refiner,* **9,** no. 4, 67 (1930).
10. Chem. Constr. Corp. B.P. 398,023 (1931).
11. —— F.P. 743,624 (1931).
12. —— F.P. 784,147 (1933).
13. Davis, W. N., and Davis, G. A. U.S.P. 1,511,721 (1924).
14. Egloff, Morrell. *Refiner,* **2,** no. 7, 5 (1923).
15. Egloff, G. U.S.P. 1,535,213 (1925).
16. Engler-Hoefer. *Das Erdöl,* **1,** 337.
17. Gilchrist. *Refiner,* **9** (9), 85 (1930).
18. Halloran, R. A., Davis, W. N., and Davis, C. A. U.S.P. 1,604,641 (1926).
19. —— —— —— U.S.P. 1,752,555 (1930).
20. Hechenbleikner, I. U.S.P. 1,264,509 (1918) and U.S.P. 1,264,182 (1918).
21. —— U.S.P. 1,900,239 (1933).
22. —— U.S.P. 1,953,225 (1934).
23. —— U.S.P. 1,953,226 (1934).
24. —— U.S.P. 958,402 (1934).
25. —— U.S.P. 1,969,793 (1934).
26. —— U.S.P. 1,991,745 (1935).
27. Hechenbleikner, I., and Oliver, T. C. U.S.P. 1,415,443 (1922).
28. —— —— U.S.P. 1,421,688 (1922).
29. —— —— U.S.P. 1,423,766 (1922).
30. —— —— U.S.P. 1,423,767 (1922).
31. Hechenbleikner, I., and Oliver, T. C. U.S.P. 1,429,140 (1922).
32. —— —— U.S.P. 1,456,874 (1923).
33. —— —— U.S.P. 1,586,801 (1926).
34. —— —— U.S.P. 1,599,360 (1926).
35. Hinde. U.S.P. 1,776,070 (1930).
36. Kalichevsky, V. A., and Stagner, B. A. *Chemical Refining of Petroleum,* American Chemical Society Monograph no. 63, 94–9 (1933).
37. —— —— Ibid. 102–3.
38. —— —— Ibid. 104–5.
39. Kauffman. *Refiner,* **7,** no. 9, 78, 83–4 (1928).
40. Landolt. *Nat. Petr. News,* **22,** no. 42, 67–9.
41. Mast, W. C. U.S.P. 1,790,507 (1931), and U.S. Reissue P. 19,064 (1934).
42. Oliver. U.S.P 1,195,075 (1916).
43. Ormandy, W. R., and Craven, E. C. *J.I.P.T.* **13,** 311–20 (1927).
44. —— —— Ibid. 844–54.
45. Robinson, C. I. U.S.P. 1,014,520 (1912), and 1,057,395 (1913).
46. Schildhaus, G., and Condrea, C. U.S P. 956,184 (1910).
47. Simonson, W. H., and Mantius, O. U.S.P. 1,384,978 (1921).
48. Southby, E. R. B.P. 1,909 (1868).
49. Spangler, S. F. *Ind. Eng. Chem.* **21,** 417–18 (1929).
50. —— *Proc. A.P.I.* **14** (iii), 106 (1933).
51. Stark, J. D. B.P. 12,028 (1889).
52. Steau Romana. G.P. 224,566 (1910).
53. Thornton, M. K., Neighbors, C. C., and Keith, J. R. *Oil and Gas J.* **28,** no. 42, 184 (1930).
54. Thornton, M. K., Wilson, E. W., and Wilson, H. W. *Oil and Gas J.* **29,** no. 11, 212–13 (1931).
55. Thornton, Frier, Francis, and McBurnett. *Oil and Gas J.* **29,** no. 12, 38, 111, 112 (1931).
56. Weir, H. M., Houghton, W. F., and Majewski, F. M. *Ind. Eng. Chem.* **22,** 1293–1300 (1930).

PETROLEUM COKE

By **W. F. STROUD, Jr.**, M.E., A.I.C.E.
Assistant Plant Manager, Atlantic Refining Company

Production, Characteristics, and Utilization

CRUDE petroleums or their various fractions, when heated above certain temperatures, which vary with the nature of the material, are subject to thermal decomposition resulting in the formation of gases, liquid fractions of different volatility from the original charge, and solid residues. The latter are classified as petroleum coke and are obtained chiefly from two types of refinery equipment.

In coking stills it has been the practice for many years to charge large cylindrical stills with heavy crude oils, topped crudes, or heavy fuel oils and supply heat at essentially atmospheric pressure until all but 4–8% of the volatile constituents are driven off as overhead products.

The residue from this destructive distillation is found on the bottom of the still as a dry porous grey mass, which may vary in thickness from 6 to as much as 30 in., depending on the character of the charge. Mechanical devices have been developed to aid in the removal of coke from this type of still, such as chains which are dragged from the still with a winch, breaking up the coke in the process. This operation is still largely manual, however, and the stills cannot be run continuously.

In the case of cracking stills, the operation of which is to-day the main source of petroleum coke, various petroleum products are rapidly heated above their decomposition temperatures and held at relatively high pressures for varying lengths of time. Most of the coke formation occurs in reaction chambers or soaking sections and, after the process has been started, is practically continuous. The yield of coke varies between wide limits, depending on the charging stock, process, and conditions of operation, and may run as high as 40 to 50 lb. per barrel. After periods, which may extend to 8 or 10 weeks, it is necessary to remove the accumulated coke from the system. The character of cracking-still coke is quite different from that formed in coking stills. It is usually black in colour, has a relatively high volatile content and is very friable, resulting in a high proportion of fines.

The Knowles coke oven, a recent development for the disposal of heavy refinery residues not saleable as liquid fuels, produces gasoline, gas oil, low viscosity fuel oil, and a coke superior in quality to that obtained from coking stills. This equipment is in part similar to by-product coke ovens, and the essential features of the process consist of a tubular preheating furnace, charging pumps and line, horizontal ovens, a vapour collecting and condensing system, a ram for removing hot coke, a special receiving car and quenching system, and a screening tower for classifying the coke into several market grades. Practically any heavy oil or tar can be pumped through the preheater at sufficiently high velocity to avoid coking in the tubes. This hot oil, which has been brought to a temperature where cracking has started and coke will form rapidly on further heating, is discharged on to the floor of horizontal, refractory-lined ovens, six to a battery, where it is coked by heat supplied to the floor of the ovens by gas burners. Each oven is connected to a large vapour header which leads to a fractionating column at the end of the battery. The entire vapour system is operated under a slight vacuum (approximately 0·2 in. of water in the ovens).

Preheated oil is sprayed on to the oven floor for about 2½ hr. and is maintained at about 850° F. during this time. The oven charge is then dried out for 2 or 3 hr., while the temperature rises to about 1,050° F. in the oven. The oven doors are then opened and an electrically-driven ram pushes the entire mass of hot coke into a special car which is hauled immediately to a quenching station, where the coke is flooded with water. Crushing, screening, and loading into cars are then accomplished with conventional equipment. A complete cycle requires about 6½ hr. The coke produced by this process is superior to that obtainable from the other two common sources in that it is drier, cleaner, more dense, and far less friable, being pre-eminently suitable for domestic heating.

The mechanism of coke formation probably involves a succession of dehydrogenations and splitting-off of light hydrocarbons from heavy oil residues until a mass is left which is not all elemental carbon but a mixture of carbon and unsaturated hydrocarbons of very high molecular weight and high carbon to hydrogen ratio. During destructive distillation, heavy oils pass through an asphalt and pitch stage in which free carbon and complex hydrocarbons are formed in colloidal suspension. Agglomeration of these colloidal particles to a fairly coarse suspension eventually results in settling out of a pitchy mass which by further decomposition produces a porous mass of coke.

In cracking stills the destructive distillation is not carried as far as in other coke-forming processes. The following proximate analyses of the three types of coke discussed above are indicative of the degree to which decomposition takes place.

Proximate Analyses

(Air-dry basis)

	Cracking-still coke %	*Coking-still coke* %	*Knowles oven coke* %
Moisture . . .	0·1–5·0	0·0–0·5	0·0–0·5
Volatile matter . .	3·5–18·0	4·0–7·0	1·0–5·0
Fixed carbon . . .	79·0–92·0	92·0–96·0	95·0–99·0
Ash	0·05–1·5	0·2–1·3	0·2–1·3
Sulphur . . .	0·2–4·0	1·0–2·5	0·7–1·6
B.Th.U. per lb. . .	15,200–16,200	14,800–15,500	14,200–15,000

The utilization of petroleum coke is quite varied. Its largest use is as refinery and general industrial fuel where its low ash content and high thermal value are particularly desirable. When removed from cracking stills approximately 75% of petroleum coke is in the form of 'breeze' and is used as powdered fuel after further pulverizing. The high volatile content of this coke ensures easy ignition, and rapid and complete combustion. There is little tendency for slagging of refractories or plugging of flues because of the low ash content. The absence of ash militates against the use of lump sizes of coke on grates or stokers because the high temperature of the coke bed tends to burn out the grates. In hand-fired furnaces, such as domestic heating units, lump coke can be used very satisfactorily by covering the grates with broken firebrick. Coking-still or Knowles-oven coke is most desirable for domestic use because of its cleanliness. A number of investigations have been carried out with a view to utilizing coke 'breeze' for domestic heating, as this will net the refiner a greater return than the sale of this material for industrial fuel. Some procedure for briquetting would seem to be the only feasible means of attaining satisfactory results. A binder is essential to give the resultant briquette sufficient firmness to stand handling. The most promising binders are some form of cracking-still tar or asphalt, which is used in quantities ranging from 1 to 5%. Briquettes made in this way stand handling fairly well, but due to the increased volatile content in the binder give a smoky fuel. Calcining green briquettes at temperatures of 900–1,000° F. serves to coke the binder and is reported to yield a clean, smokeless, strong fuel.

Petroleum coke has proved to be a particularly desirable source of carbon for the manufacture of electrodes because of its low content of impurities. In electrolytic processes, such as the reduction of alumina to aluminium, production of magnesium and sodium, the electrodes come in direct contact with the reduced metal, and any impurities in the electrode may appear in the finished product. Specifications for petroleum coke to be manufactured into carbon products vary in the limitations as to impurities and volatile matter permissible, but approximate the following limits:

Volatile matter . . .	10·0% max.
Ash	1·0 ,,
Sulphur	1·0 ,,
Soluble salts	0·5 ,,
Total silica and iron oxide .	0·2 ,,

This practically restricts the source to coke of the coking-still type, which on receipt from the refinery is crushed to small size, oven dried to remove moisture, and then calcined at a high temperature (900–1,000° C.). The heat treatment drives off volatile matter, reduces subsequent shrinkage of the coke, and makes the material graphitic, thereby reducing its electrical resistance. After grinding to a fine powder the carbon is mixed with a binder, tamped into moulds under high pressure, and subsequently baked at a high enough temperature (900° C. or more) to remove all volatile matter from the binder. Electrodes up to 2 ft. in diameter have been made by this procedure.

The aluminium industry is probably the largest consumer of carbon electrodes made from petroleum coke, and also uses a considerable tonnage for lining the electric furnaces. Approximately 1 lb. of petroleum coke is reported as being consumed for each pound of aluminium produced.

In addition to the electrolytic uses of petroleum coke, a number of other industries employ this type of material for electro-thermal work, where a high degree of purity is required. Outstanding examples are to be found in the manufacture of silicon and boron carbide abrasives and calcium carbide. In the first-mentioned application a core of granulated carbon acts as a resistor in developing heat in the furnace, and a surrounding mixture of coke and sand react to form the abrasive. Under some conditions of operation artificial graphite is formed. Calcium carbide is formed by reducing powdered lime in an electric furnace with an excess of powdered coke. The liberated metallic calcium combines with the carbon to form the desired product. A very low sulphur and phosphorus content is necessary in order that acetylene made from the carbide will not contain hydrogen sulphide or phosphine in noticeable quantities.

Other uses of petroleum coke include its application as a reducing agent in the preparation of lithopone and 'blanc fixe' which are used as pigments in paint manufacture, in various metal refining industries to reduce oxide formation, and as a recarbonizing agent in some branches of the iron and steel industry. The ceramic industries employ coke to a limited extent as a powdered fuel in rotary cement kilns, in the burning of lime, and for burning brick where it is desired to impart definite colours to the product by reduction of the metal oxides in the clay without leaving ash in the brick. Small amounts of petroleum coke are also used by a very diverse group of industries particularly where the source of supply is nearby.

The production of petroleum coke in the United States was not very large until the introduction of cracking units on a commercial scale. Prior to 1917 or 1918 practically all the coke produced came from coking stills, and the production from this source has remained relatively constant in volume. The following tabulation of annual production for the 15 years from 1918 to 1932 illustrates the increasing importance of cracking stills as a source of coke.

Thousands of Short Tons

(As reported by the Bureau of Mines)

1918	560
1919	603
1920	577
1921	604
1922	707
1923	673
1924	761
1925	991
1926	955
1927	1,140
1928	1,425
1929	1,827
1930	1,931
1931	2,035
1932	1,788

Petroleum coke cannot be produced profitably except as a by-product of processes yielding materials of much greater unit value. In cracking-still operations the formation of coke is purely incidental, usually undesirable, and the refiners desire to reduce it to a minimum. With coking stills the primary object is to convert heavy residual materials into products which can be readily handled and are saleable, while with Knowles ovens the production of good coke is essential to the success of the operation. At the present time the tonnage of coke produced is greatest in amount from cracking stills and least from Knowles ovens which are a recent development.

The economics of coke production is closely associated with the broader aspects of petroleum refining, and since coke is a by-product it is greatly influenced by the relative value of the products which are made by alternative methods of processing the charging stock and the relative value of the other products which are produced simultaneously. If the charging stock is saleable as such and has a definite commercial value, then the coking still must compete for the production on the basis of monetary return for the coke and distillate products from which the cost of the coking operation must be deducted. If the refinery has available coke-still charging stock which because of the presence of excessive colloidal carbon or other material is unfit for sale as such, the alternative value of the material as a coking stock may be reduced accordingly and permit the production of coke on a competitive basis.

PROPERTIES OF PETROLEUM COKE

By D. W. GOULD

THE solid porous residue resulting from distillation of an oil to dryness or from cracking of an oil with attendant deposition of carbon is termed petroleum coke. The composition and other properties depend upon the origin of the stock as well as the duration and intensity of the coking or cracking treatment. Only an imperfect correlation of the amount of coke resulting from a stock of known properties has been made; no correlation between the properties of the oil and the product coke can be made. An enumeration of the characteristics of any coke must be unique, but it is believed that such a summary is valuable in approximating the description of other cokes, in the same manner that the behaviour of bituminous coals of different geographical origin are compared and prejudged by common and easily determined tests.

Ultimate Analysis of Coke.

It is not to be expected that the ultimate analysis of coke should be significant, because, like volatile matter determinations in a proximate analysis, the residual hydrogen will reflect the severity of thermal conditions to which the coke has been subjected. Trusty [11, 1932] gives a comparison of the two methods of analysis upon a single coke.

Proximate		*Ultimate*	
Moisture	0·35%	C	97·3%
Volatile matter	7·7%	H	1·2%
Fixed carbon	90·8%	N	0·2%
Ash	1·15%	S	1·0%
B.Th.U. per lb.	15,490	O	0·3%

The fusing-point of ash from a single coke is said [5, 1930] to be 2,000° F., although this must be a function of the ash in the original crude, influenced, of course, by foreign matter accidentally introduced as scale from steel or mineral matter from clay used as luting in coking operations.

Proximate Analyses of Petroleum Cokes

(*a*) *Cracking Still Cokes*

Analyses as weight per cent.

Crude oil source	*Moisture*	*Volatile matter*	*Fixed carbon*	*Ash*	*Sulphur*	*Heating value (B.Th.U. per lb.)*	*Authority*
Mid-Continent	0·50	8·07	91·81	0·05	0·83	15,645	7
"	0·30	12·93	85·63	1·14	1·44	15,300	7
"	1·07	10·83	87·65	0·45	0·87	15,568	7
Texas	0·15	15·02	83·21	1·62	1·96	15,456	7
Panhandle, Texas	3·31	14·00	81·12	1·59	0·45	15,573	7
Smackover, Texas	0·11	12·28	87·15	0·46	4·18	15,898	7
" "	3·33	17·02	79·20	0·45	3·70	15,454	7
Kentucky	0·39	11·65	87·42	0·54	0·66	16,403	7
Pennsylvania	0·20	11·39	87·42	0·99	0·22	16,248	7
"	0·46	10·07	88·92	0·05	0·50	15,573	7
California	0·47	18·03	80·49	0·91	1·09	15,295	7
"	1·48	13·84	82·29	1·00	1·39	15,322	7

(*b*) *Coking Still Cokes*

Analyses as weight per cent.

	Moisture	*Volatile matter*	*Fixed carbon*	*Ash*	*Sulphur*	*Heating value (B.Th.U. per lb.)*	*Authority*
	0·6	2·1	95·8	1·5	0·5	14,480	7
	0·3	3·9	94·1	1·0	0·7	14,900	7
	0·5	13·0	85·0	0·5	0·5	..	7
	0·3	8·0	90·5	1·0	0·5	..	7
Mid-Continent and East Texas Reduced Crudes plus Heavy Cracking Still Tar	0·39	10·31	88·07	1·23	1·23	15,330	1
	1·30	9·84	88·20	0·66	1·01	15,100	1
	0·64	8·96	89·39	1·01	0·94	15,050	1
	1·80	11·26	86·10	0·84	0·76	15,510	1

(*c*) *Oven Coke* (i.e. made in vessel constructed of refractory material)

Analyses as weight per cent.

Source of charge	*Moisture*	*Volatile matter*	*Fixed carbon*	*Ash*	*Sulphur*	*Heating value (B.Th.U. per lb.)*	*Authority*
Dubbs Cracking Still	1·1	5·2	92·85	0·85	1·15	14,515	1
Cross Still Tar	0·3	7·3	92·20	0·2	1·52	14,650	1
" "	0·3	7·4	91·80	0·5	0·86	14,700	1
Mid-Continent Vacuum Still Bottoms	0·6	2·76	94·84	1·8	1·23	14,400	1
	0·0	1–3	96–99	0·5	1·0–1·5	14,500	3

Physical Properties.

Petroleum coke may at times possess outward physical characteristics which render extremely difficult its identification from the product resulting from coking of coal or coal tar. Its colour and lustre may range from intense black to the bright silvery appearance found in the best metallurgical coke. It may have the high metallic ring of high-temperature coke. Its streak is black; the hardness may be as high as 6 (Moh's scale). Its fracture is irregular as in coke from coal. Its apparent density may be as low as 0·74 and its true density as high as 1·52. The high percentage of cellular space accounts in part for the ignition and burning characteristics.

Coke source	*Apparent density*	*True density*	*Cellular space, %*	*Authority*
(1) Mid-Continent	1·131	1·286	12·1	7
(2) „	0·737	1·376	46·8	7
(3) California	0·851	1·305	34·8	7
(4) Pennsylvania	0·866	1·415	38·8	7
(5) „	0·95	1·52	37·5	2

The shatter test (A.S.T.M. Standard Method 2,738 (1930)) reveals that the coke may possess strength comparable to by-product oven coke. The above cokes were tested.

Sample	*2 in.*	*1½ in.*	*1 in.*	*½ in.*	*Fines*	*Loss*
(1)	73·2	20·4	2·0	1·9	2·5	..
(2)	93·9	0·0	0·0	2·3	1·1	0·3
(3)	0·0	11·0	32·5	27·5	27·5	1·5
(4)	60·0	3·5	6·0	10·0	18·5	2·0
(5)	89–93	2·5–3·5	..	..	..	..
Southern B.P.	92·5	4·5	..	..	..	..
Western B.P.	82·5	8·0	..	..	..	..

Schulz [10, 1930] found marked differences in combustion of either lump or pulverized coke derived from different types of refinery operation. He states that coke from non-residuum operation burns more rapidly and produces higher localized furnace temperatures when burned under the same conditions. The marked difference in the proximate analyses, however, would possibly account for variation in burning characteristics.

	Coke from residuum operation	*Coke from non-residuum operation*
Moisture	0·38	0·35
Ash	1·90	0·67
Volatile matter	11·65	18·89
Fixed carbon	86·45	80·44
Sulphur	1·00	1·10
B.Th.U. per lb.	15,400	15,450

Carpenter [2, 1934] gives data upon coke intended for foundry use in competition with by-product oven coke.

	Petroleum coke	*Southern B.P. coke*	*Western B.P. coke*
Ignition temp., ° C.	475–492	630–680	645–680
Maximum temp., ° C.	702–738	800–860	783–838
Rise in temp., ° C.	220–248	170–180	138–158
Time for burning, min.	8–9	8–9	9+
Ash	0·33–1·5	10·2	12·9
B.Th.U. per lb.	14,400	12,580	12,610

The low ash-content of petroleum coke necessitates caution in protecting grates from intense local heating, but the use of this fuel in pulverized form is feasible. It is probable that the large surface and reactive nature of the coke offset the disadvantages of low volatile matter. Mekler [6, 1930] describes a test with pulverized coke used in a commercial boiler.

Proximate analysis of coke as fired:

Moisture	6·56%
Volatile matter	15·40%
Fixed carbon	77·47%
Ash	0·47%
B.Th.U. per lb.	14,712

Performance:

Actual water evaporated, lb. per hr.	41,070
Equivalent evaporation, lb. per hr.	44,648
„ „ per lb. fuel	12·19
Flue-gas temp., 550° F. (288° C.):	
CO_2 in flue gas	15·03%
O_2 „ „	4·68%
CO „ „	0·0%
Boiler efficiency without economizer	80·5%
Comparative efficiency with economizer	86·07%
K.W.H. to pulverize 1 ton coke	21·1

Nugey [8, 1934] says that petroleum coke responds well to activation treatment, but does not give conclusive data upon the characteristics of the activated coke.

Graphitization of petroleum coke can be effected by metals; and Schleifstein [9, 1928] describes the relative catalytic effect of several elements. The coke was ground in a ball mill to pass 200-mesh and was calcined at 1,100° C. (2,012° F.). The residue had a specific gravity 1·99–2·05 and an ash-content of 0·3%. A product made by baking admixtures of coke and finely divided metals approached Ceylon graphite in resistivity.

Material	*Resistance at 30° C. (ohms per cu. in.)*
Ungraphitized petrol. coke (0·3% ash)	0·00174
Graphitized petrol. coke	0·000860
Acheson graphite	0·000350
Ceylon graphite	0·000265
Graphitized petrol. coke plus 4% Ca	0·000610
„ „ „ 5·5% Mn	0·000536
„ „ „ 2·4% Mg	0·000471
„ „ „ 2·7% Al	0·000400
„ „ „ 5·5% Fe	0·000370
„ „ „ 5·8% Ni	0·000380
„ „ „ 5·0% Cr	0·000320
„ „ „ 1·1% B	0·000290

The use of petroleum coke for manufacture of electrodes has led to the discovery of the effect of temperature upon the properties of the coke. Hansen [4, 1909] compared graphite, lamp-black, and petroleum coke as electrode material. Each material was used as a powder ground to pass 200-mesh and bonded with about 40% pitch by baking. Petroleum coke exhibited properties intermediate between those of graphite and lamp-black. The apparent and absolute densities approach 1·6 and 2·2 respectively, with temperatures above 2,000° C. The resistance varied with temperature of firing, as follows:

Temp. of firing, ° C.	*Resistance (ohms per cu. in.)*
500	0·009
750	0·004
1,500	0·0015
3,000	0·001

REFERENCES

1. Campbell, O. F. *Oil and Gas J.* **33**, no. 45, 68 (1935).
2. Carpenter, C. B. *Mechanical Engineering*, **56**, 330 (1934).
3. Foster, A. L. *Nat. Petr. News*, **25**, no. 10 (1933).
4. Hansen, C. A. *Trans. Amer. Electrochemical Society*, **25**, 279 (1909).
5. Lima, D. O. *Nat. Petr. News*, **22**, no. 31, 81 (1930).
6. Mekler, L. A. *Nat. Petr. News*, **22**, no. 47, 51 (1930).
7. Morrell and Egloff. *Chem. and Ind.* **51**, 467 (1932).
8. Nugey, A. L. *Refiner*, **13**, no. 2, 49 (1934).
9. Schleifstein, M. L. *Canadian Chemistry and Metallurgy*, **12**, no. 3, 59 (1928).
10. Schulz, M. E. *Refiner*, **9**, no. 1, 55 (1930).
11. Trusty, A. W. *Refiner*, **11**, no. 10, 519 (1932).

SYNTHETIC DERIVATIVES FROM PETROLEUM

CHLORINATED COMPOUNDS AND DERIVATIVES

THE ADDITION OF HALOGENS TO OLEFINE BONDS

By Professor H. B. HASS, Ph.D.

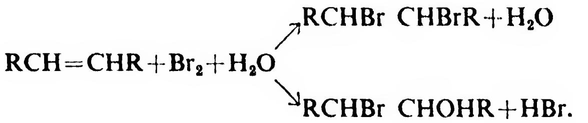
Head, Department of Chemistry, Purdue University

Introduction

THE olefines and other compounds possessing an ethylene bond are characterized by their power of reacting additively with the halogen elements. This phenomenon has been known since 1795, when ethylene dichloride was first prepared [8], but only recently has become of major importance as a means of the industrial synthesis of certain dihalides. The ready availability of the lower olefines, which occur abundantly in cracking-still gases, and the low cost of chlorine have led to the present importance of ethylene dichloride as an inexpensive chlorinated solvent and an important material for organic synthesis. Ethylene dichloride is used with the corresponding dibromide as the means of supplying the halogens necessary to unite with the lead when tetra-ethyl lead is used as a suppressor of detonation in motor fuels. Propylene dichloride is also available in tank-car quantities, but its greater instability to heat and more rapid hydrolysis rate limit its uses for some purposes.

Analytical Uses of the Olefine-Halogen Addition

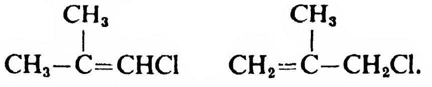
This reaction has been widely used as a means for the quantitative determination of olefinic bonds. Thus the Hanus method [12, 1901–2] employs iodine monobromide dissolved in glacial acetic acid, that of McIlhiney [20, 1899] uses bromine dissolved in carbon tetrachloride, while Francis [10, 1926] utilized the bromine liberated by the action of dilute sulphuric acid upon an aqueous solution of sodium bromide and sodium bromate. By this last technique the concentration of bromine is maintained at a constant low value, and there is much evidence that this condition greatly minimizes substitution reactions. Francis points out that the presence of water is not a disadvantage, even though no mutual solvent is used to render it miscible with the gasoline or other hydrocarbon being tested, provided vigorous agitation is employed. The addition of hypobromous acid to the olefine, which is a competing reaction, does not affect the results, since it requires the same quantity of bromine as does simple addition.



$$RCH{=}CHR+Br_2+H_2O\begin{array}{l}\nearrow RCHBr\ CHBrR+H_2O\\ \searrow RCHBr\ CHOHR+HBr.\end{array}$$

More recently a saturated aqueous solution of iodine tribromide has been utilized for the rapid absorption of propene [22, 1933].

The principal difficulties involved in all these procedures are (*a*) substitution reactions are difficult to eliminate, (*b*) reaction may be incomplete, and (*c*) results vary with the conditions of the experiment. Thus Kondakoff [17, 1891] has shown that olefines which react readily with mineral acids (usually those capable of thus forming tertiary halides) yield substitution products in addition to, or instead of, undergoing addition. Thus isobutene yields isocrotyl chloride and isobutenyl chloride, having the following structures respectively:



$$CH_3-\overset{\overset{CH_3}{|}}{C}{=}CHCl \qquad CH_2{=}\overset{\overset{CH_3}{|}}{C}-CH_2Cl.$$

Bromine shows less tendency to substitute than chlorine, and the substitution reaction is more or less suppressed by low temperatures, but even on treatment with bromine at 0–5° C. isobutene yielded, according to Hurd and Spence [14, 1929], only 65·5% of the expected dibromide with 25·5% tribromide and 9·0% of still more highly brominated products.

Mechanism of the Reaction

Although ordinary laboratory experience with impure materials would lead one to suppose that the addition of bromine to olefines is practically instantaneous, Davis [5, 1928] showed that, after careful purification and drying, ethylene and bromine require several days to react, while several hours are necessary for the bromination of propene. The reaction rate is markedly increased by the presence of a trace of moisture, and Davis postulated a mechanism involving a hydrate of bromine, $Br_2 \cdot H_2O$, as the intermediate. This hypothesis also explained the negative temperature coefficient, i.e. the fact that reaction is far more rapid at 0° C. than at 25°, since it might be supposed that the hydrate is decomposed at the higher temperature. Davis's hypothesis does not, however, explain why the reaction should have an induction period during which reaction is relatively slow; the discovery that the second 25% of the olefine reacts in less time than the first 25%, even in fairly concentrated solutions, led Williams [28, 1932] to conclude that some product of the reaction is the catalyst. Experiments showed that hydrogen bromide is a very powerful positive catalyst, the reaction becoming too rapid for accurate measurement when a little is added. Since hydrogen bromide might be formed by the action of bromine with water, the lesser catalytic effect of water is thus explained. Williams confirmed Davis's discovery of the negative temperature coefficient and interpreted it on the assumption that the intermediate is the loose, molecular addition compound, $C_2H_4 \cdot HBr$, formed from ethylene and hydrogen bromide, and previously reported by Maass and Wright [19, 1924].

Davis also observed that different olefines show very different reaction rates with bromine, that light greatly accelerates the reaction, and that in the presence of light the differences between the reaction rates of various olefines are not nearly so striking as they are in the dark.

When gaseous ethylene and bromine are mixed and allowed to combine at either 0° C. or room temperature, reaction occurs at the glass surface of the containing flask. Depending upon conditions, the addition of bromine and ethylene may behave as a zero-order, first-order, or second-order reaction. The transition from a second-order to a first-order reaction is favoured by (*a*) a wet surface, (*b*) relatively high initial pressures of bromine, (*c*) low temperature. The fact that oxygen, nitrogen, and air retard the reaction was interpreted as indicating the existence of a chain mechanism which starts on the glass and extends to vapour phase.

Stewart and Smith [24, 1929] observed that the addition of chlorine to ethylene likewise takes place at the glass surface of the containing vessel when the reactants are gaseous. When the ethylene and chlorine are thoroughly dry and pure the reaction is autocatalytic. Substitution occurs as well as addition, and the presence of gaseous oxygen tends to retard both reactions, but especially the substitution. The presence of liquid ethylene dichloride or trichloroethane catalyses the reaction positively. In a later paper Stewart and Smith [25, 1930] postulate the following mechanisms, the asterisks indicating an activated form of the compound:

$$\begin{aligned}
&C_2H_4(\text{gas})+Cl_2(\text{gas}) \xrightarrow{\text{catalyst}} C_2H_4Cl_2{}^*\\
&C_2H_4Cl_2{}^*+C_2H_4+Cl_2 \rightarrow 2C_2H_4Cl_2\\
&C_2H_4Cl_2{}^*+Cl_2(\text{gas})\\
&\qquad\qquad \rightarrow C_2H_3Cl_3{}^*+HCl\\
&\qquad\qquad \xrightarrow{\text{deactivator}} C_2H_3Cl_3(\text{gas})+HCl(\text{gas})\\
&C_2H_3Cl_3{}^*+C_2H_4+Cl_2\\
&\qquad\qquad \rightarrow C_2H_3Cl_3{}^*+C_2H_4Cl_2{}^*\ldots+58{,}100 \text{ calories}\\
&C_2H_4Cl_2{}^* \xrightarrow[\text{wall}]{O_2} C_2H_4Cl_2(\text{gas})+36{,}400 \text{ calories.}
\end{aligned}$$

The efficiency of propagation of the chains must be very low or explosions would occur more readily than they do. A large excess of either reactant may serve to dissipate the energy of the activated molecules and thus to retard the induced reaction.

> 'According to this picture of the mechanism there is no essential difference between the thermal and the induced reactions. Photons, or any other source of activation within the liquid phase, might induce the reaction, and there is evidence that light induces a gas-phase reaction under the conditions of the present experiments. Of particular importance is the idea that by this mechanism energy *need* not be transferred at all from one molecule to another to induce the rate-determining step of the reaction. The presence of the liquid film brings about a faster reaction either by permitting the surface-formed intermediate to escape from the surface with its energy, thereby initiating a reaction chain within the liquid, or receives this energy by transfer with the same result.'

Another view of the role of oxygen as inhibitor is given by the researches of Leermakers and Dickinson, who studied the addition of chlorine to tetrachloroethylene. Here the complication of a substitution reaction is eliminated and only one product results from the reaction in the absence of oxygen. The situation was further simplified by using monochromatic light of λ 4,358 which activates only the chlorine, since it is not absorbed by the chloro-olefine or the oxygen. The combination is markedly inhibited by the presence of free oxygen, and if sufficient oxygen is present, the products consist exclusively of oxygenated derivatives, trichloroacetyl chloride and phosgene, in spite of the fact that it is the chlorine which is being activated by the light.

$$\begin{gathered}
C_2Cl_4+Cl_2 \rightarrow C_2Cl_6\\
2C_2Cl_4+O_2 \rightarrow 2CCl_3\cdot COCl\\
C_2Cl_4+O_2 \rightarrow 2COCl_2.
\end{gathered}$$

In the absence of oxygen the results may be interpreted by the following chain mechanism:

$$\begin{gathered}
Cl_2+h\nu \rightarrow 2Cl\\
Cl+C_2Cl_4 \rightleftharpoons C_2Cl_5\\
C_2Cl_5+Cl_2 \rightarrow C_2Cl_6+Cl\\
2C_2Cl_5 \rightarrow 2C_2Cl_4+Cl_2 \text{ (or } C_2Cl_6+C_2Cl_4\text{).}
\end{gathered}$$

Under the conditions of the experiments one quantum of light caused from 300 to 2,500 molecules to react in the absence of oxygen, while in its presence only 1–3 molecules reacted per quantum absorbed. The inhibition of the reaction is thus caused by the energy of the free chlorine atoms being utilized in some way for the promotion of the oxidation. In this way the reaction chains are broken.

Deanesley [6, 1933; 7, 1934], by a careful exclusion of free oxygen, has been able to utilize the addition reaction as a means of initiating reaction chains which result in the substitutive chlorination of co-present saturated hydrocarbons. Thus a mixture of 10% of butene and 90% butane may be chlorinated to a mixture of monochlorides and dichlorides of butane. This would seem to be more consistent with the mechanism of Leermakers and Dickinson than with that of Stewart and Smith, since in the latter case it was assumed that reaction might occur without the transfer of energy from one molecule to another. Although the mode of initiation of the reaction chains by absorption of light could not occur under Deanesley's conditions, it seems certain that any mechanism which would produce monatomic chlorine molecules would result in substitutive chlorination. On the other hand, Deanesley did not observe that the addition of chlorine to butene was retarded appreciably by the presence of free oxygen, although the substitutive halogenation was very greatly inhibited. This interesting selective inhibition suggests the possibility that the vigorous agitation advocated by Francis in the analytical bromination of olefines may have contributed to the precision of the results by maintaining a maximum concentration of free oxygen.

Industrial Processes

Ethylene dichloride may be produced by the combination of ethylene and chlorine under a variety of conditions. The process patented by Curme [3, 1912, 1919, 1921] consists in allowing dry chlorine to react with ethylene in liquid phase at temperatures below 0° C., under a pressure corresponding to the vapour-pressure of the chlorine. The low temperature and absence of light suppress the formation of more highly chlorinated materials, while the absence of moisture largely eliminates corrosion difficulties. It is desirable to use ethylene which is relatively free from propylene or, of course, the product will be contaminated with the less stable propylene dichloride.

Another process is that of Mersereau [21, 1924, 1925]. In this procedure ethylene and chlorine are mixed in gaseous phase and allowed to rise through a reaction tower. The temperature is controlled by a spray of cold water or chlorinated hydrocarbons which travels countercurrently to the gas. The exit gases are passed through a condenser and the condensate returned to the base of the tower. In case water is used as the cooling liquid, it is separated by decantation from the chlorinated products as they leave the base of the tower.

Strosacker [26, 1930] has advocated the use of antimony pentachloride dissolved in ethylene dichloride as the chlorinating agent. This compound is converted to antimony trichloride in the process, and the latter is easily rechlorinated to the pentachloride. It is stated that no substitution reactions occur when this procedure is used.

Ethylene dibromide may be produced by the addition of bromine to ethylene or by the combination of hydrogen bromide [2, 1925; 27, 1931] with either acetylene or vinyl bromide. The actual production, at least in the U.S.A., has been through the former synthesis. This product utilized most of the 9 million pounds of bromine produced in that country in 1931. Ethylene dibromide and ethylene dichloride are used with tetra-ethyl lead in 'ethyl' gasoline. Because of the increasing demand for motor fuel of high octane number, the bromine production has recently been augmented by the erection of a plant of a capacity of 20 million pounds per annum for extracting the element from sea-water. Conversion of bromine to ethylene dibromide is said to take place 'according to the standard method [23, 1934] to form pure ethylene dibromide . . . at an efficiency somewhat over 90%'. The 'standard method' referred to is presumably the liquid-phase reaction produced by dissolving ethylene in an excess of bromine. When carried out in the laboratory as an exercise in elementary organic chemistry, the bromine is covered with water to prevent undue losses by evaporation, and the heat of the reaction is removed by immersing the absorption apparatus in cold water. The corrosive nature of bromine-water might be expected to lead to the large-scale manufacture being conducted under substantially anhydrous conditions, since Williams has shown that hydrogen bromide rather than water appears to be the necessary catalyst.

The production of ethylene dibromide from acetylene by the addition of 2 molecules of hydrogen bromide is a possibility in locations where ethylene is more expensive than the former hydrocarbon. This would appear to be contrary to Markownikoff's rule, which states that halogen acids add to olefines in such a way that the halogen attaches itself to the least hydrogenated carbon atom, and, in fact, Kharasch, McNab, and Mayo [16, 1933] have shown that the 'normal' reaction proceeds as follows, yielding first vinyl bromide and secondly 1,1-dibromoethane:

$$(1)\ C_2H_2 + HBr \rightarrow CH_2{=}CHBr$$
$$(2)\ CH_2{=}CHBr + HBr \rightarrow CH_3{\cdot}CHBr_2.$$

Statements in the literature concerning the products of the addition of hydrogen bromide to vinyl bromide are extremely conflicting (e.g. see the article by Wibaut [27, 1931]), and according to Kharasch the factor which accounts for these divergent results obtained by former workers is the 'peroxide effect'. Thus, in the absence of peroxides or substances such as free oxygen which are capable of yielding peroxides, the reaction yields practically 100% 1,1-dibromoethane. In the presence of oxygen or peroxides the reaction may yield 100% ethylene dibromide. Solvents, temperature, light, anti-oxidants, and different salts and surfaces exert their specific effect not upon the organic molecule itself, but either upon the peroxide molecules or in activating oxygen liberated by the decomposition of peroxides. Similar relationships hold for many other additions of hydrogen bromide to olefinic bonds, but it is interesting to note that peroxides do not affect the addition of hydrogen iodide or hydrogen chloride. In the case of hydrogen iodide its powerful reducing action eliminates peroxides from the reaction zone, but the reason for the absence of 'peroxide effect' in the additions of hydrogen chloride to olefines is still entirely obscure. The statement from the patent literature that ethylene dibromide can be produced by reaction between acetylene and hydrogen bromide in the vapour phase in the presence of oxidizing gases such as air, oxygen, nitrogen peroxide, and ozone [11, 1929] is doubtless correct, and this observation seems to comprise the first recognition of the importance of oxidants as catalysts in this reaction.

Propylene dichloride (1,2-dichloropropane) may be produced by the same general methods which have been noted in the case of ethylene dichloride. For instance, Curme [4, 1919] has described a process in which liquid chlorine reacts with liquid propylene in the presence of an inert diluent such as carbon tetrachloride or propylene dichloride itself. An excess of propylene is used to minimize the formation of substances more highly chlorinated than the dichloride.

Propylene dichloride is a colourless liquid boiling at 96·8° C., having a density of 1·166 and refractive index of 1·4388. Its chemical and physical properties resemble those of ethylene dichloride except for the difference caused by the presence of the secondary chlorine atom which leads to lesser stability and greater ease of hydrolysis. Its use has been suggested as a solvent for removing acetic acid from aqueous solution [13, 1933]. It has been found effective as a fumigant against the larvae of the European corn-borer [9, 1933] (*Pyrausta nubilalis* Hubn.). It is more inflammable than ethylene dichloride, and when mixed with air in suitable proportion can develop more explosion pressure in a closed bomb test than is produced by methane-air mixtures [15, 1933].

The homologues of ethylene dichloride of more than 3 carbon atoms have not assumed any considerable industrial importance, although many of them are very easily prepared. The presence of chlorine in secondary and/or tertiary positions causes a more or less pronounced tendency to split out hydrogen chloride upon distillation, and this effect becomes greater with increasing distillation temperature as we ascend the homologous series. The dichlorides of butane and of isopentane were of interest at one time as raw materials for the production of 1,3-butadiene and isoprene respectively, which were looked upon as possibilities for the production of synthetic rubber. Because of the present low prices of natural rubber, the appearance of Duprene (polymerized 2-chloro-1,3-butadiene), and the development of other processes for making diolefines, it does not seem likely that synthetic rubber will be made from olefine dichlorides.

In the conversion of certain higher olefines, such as trimethylethylene, to dichlorides where, as noted above, the suppression of substitution is a matter of considerable difficulty, the following procedure has been employed by the Badische Anilin- und Soda Fabrik. Sulphuryl chloride, SO_2Cl_2, is gradually introduced with stirring, into an excess of trimethylethylene, the temperature being maintained at -2 to 0° C.; after a further period of agitation, the sulphur dioxide and the excess of amylene are distilled off and the residue rectified in a vacuum. The sulphur dioxide is recovered and used to form more sulphuryl chloride. The formation of substitution products is said to take place to only a very small extent. At present, however, amylene dichlorides are available as a by-product of the chlorination of pentanes at a price which makes them the most inexpensive chlorinated solvent. It would seem that further research may indicate additional uses for this product.

REFERENCES

1. Badische Anilin- und Soda Fabrik. F.P. 433,309 (1911); *J.S.C.I.* **31**, 151.
2. Bauer, W. U.S.P. 1,540,748 (1925), G.P. 368,467; F.P. 546,163.
3. Curme, G. O. *Chem. Met Eng.* **25**, 999 (1921); U.S.P. 1,315,542 (1912) and 1,315,545 (1919).
4. —— U.S.P. 1,315,547 (1919); *J.S.C.I.* **38**, 848A (1919).
5. Davis, H. S. *J.A.C.S.* **50**, 2769 (1928).
6. Deanesley, R. M. F.P. 745,543 and 745,544 (1933); *Chem. Abs.* **27**, 240 (1933); C.P. 338,210 (1933).
7. —— *J.A.C.S.* **56**, 2501 (1934).
8. Dflman, Bondt, van Troostwyk, and Lauwrenburgh. *Crelles Annalen*, **2**, 200 (1795).
9. Dibble, C. B. *J. Econ. Ent.* **26**, 893–5 (1933); *Chem. Abs.* **27**, 5879.
10. Francis, A. W. *Ind. Eng. Chem.* **18**, 821 (1926).
11. G.P. 394,194 (1929).
12. Hanus, J. *Z. Nahr.- u. Genussm.* **4**, 913 (1901); *J.C.S.* (Abs.) **82** (2), 112 (1902).
13. Hartman, W. H. U.S.P. 1,908,239 (1933): assigned to Eastman Kodak Co.
14. Hurd, C. D., and Spence, L. U. *J.A.C.S.* **51**, 3561 (1929).
15. Jones, G. W., Miller, W. E., and Seaman, H. *Ind. Eng. Chem.* **25**, 771 (1933).
16. Kharasch, M. S., McNab, M. C., and Mayo, F. R. *J.A.C.S.* **55**, 2521 (1933).
17. Kondakoff, J. *Ber.* **24**, 929 (1891).
18. Leermakers, J. A., and Dickinson, R. G. *J.A.C.S.* **54**, 3853 and 4648 (1932).
19. Maass, O., and Wright, C. H. *J.A.C.S.* **46**, 2664 (1924).
20. McIlhiney, P. C. *J.A.C.S.* **21**, 1084 (1899).
21. Mersereau, G. U.S.P. 1,509,603 (1924); *Chem. Abs.* **19**, 168 (1925).
22. Roginski, S. Z., and Rathmann, F. H. *J.A.C.S.* **55**, 2800 (1933).
23. Stewart, L. C. *Ind. Eng. Chem.* **26**, 361 (1934).
24. Stewart, T. D. and Smith, D. M. *J.A.C.S.* **51**, 3082 (1929).
25. —— —— *J.A.C.S.* **52**, 2869 (1930).
26. Strosacker, C. J. U.S.P. 1,754,656 (1930); *Chem. Abs.* **24**, 2755 (1930).
27. Wibaut, J. P. *Rec. trav. chim.* **50**, 313 (1931).
28. Williams, D. M. *J.C.S.* 2911 (1932).
29. —— *J.C.S.* 1747 (1932).

GLYCOLS AND RELATED COMPOUNDS FROM OIL GAS OLEFINES

By BENJAMIN T. BROOKS, Ph.D., M.Inst.P.T.

Consulting Chemical Engineer

THE advent of cracking for gasoline made available large quantities of by-product gas rich in the simpler olefines. Cracked oil gas for gas enrichment had long been known as Pintsch gas; but the chemical utilization of the simple olefines came only with the improvement of large-scale cracking.

The glycols and related derivatives of the simpler paraffin hydrocarbons have long been known. Interest in their production on an industrial scale was greatly stimulated during the World War by the fact that ethylene chlorohydrin can easily be converted to the now well-known mustard gas, dichloro-ethyl sulphide. The interest in the use of dinitro-ethylene glycol, with nitroglycerine, in low-freezing dynamite also was a factor in the commercial development of the glycols. The use of ethylene glycol as an anti-freeze fluid for automobile radiators and the industrial uses of related products such as ethylene dichloride, ethylene oxide, and ethanolamines came later, after 1924, with the manufacture of ethylene glycol on a large commercial scale from ethylene derived from oil gas.

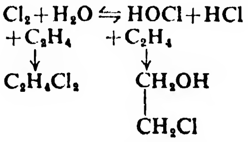
This development has been favoured in the United States by a period of unusually low-priced petroleum, the commercial installation of so-called vapour-phase oil-cracking processes giving relatively large yields of by-product gas rich in olefines, by low-priced electrolytic chlorine, and by the development of efficient methods for the separation of the olefines in oil gas so that pure chemical products could be produced.

During the World War the ethylene required for the manufacture of mustard gas was made by the catalytic decomposition of ethyl alcohol. In the United States ethylene is made in this way for the manufacture of ethylene dibromide and ethyl chloride for tetra-ethyl lead and Ethyl Fluid.

The separation of nearly pure ethylene from oil gas is advantageous on account of the purity of the resulting glycol and other products. The normally gaseous hydrocarbons can best be separated by fractional distillation at low temperatures. Ethylene can thus be separated from a typical oil gas containing 28 to 30% ethylene in a purity of 98+%, the small impurity being ethane. The recovery of the ethylene from such a gas is about 90%. This method of separation was originally proposed by Claude [18, 1929] for the purification of hydrogen from coal gas. Absorption in a solvent and fractionation under pressure in the presence of a solvent has been described by Curme [21, 1922].

The processes which are of greatest industrial interest are as follows:

(1) The reaction of ethylene with chlorine and hypochlorous acid, or cold chlorine water, as first carried out experimentally by Gomberg [36, 1919].

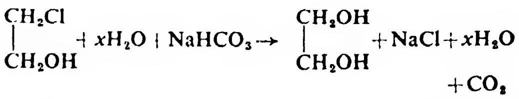


$$\begin{array}{ll} \mathrm{Cl_2+H_2O} \leftrightharpoons & \mathrm{HOCl+HCl} \\ \mathrm{+C_2H_4} & \mathrm{+C_2H_4} \\ \downarrow & \downarrow \\ \mathrm{C_2H_4Cl_2} & \mathrm{CH_2OH} \\ & | \\ & \mathrm{CH_2Cl} \end{array}$$

Both ethylene chlorohydrin and ethylene dichloride are produced, the latter in increasing proportions as the accumulation of hydrogen chloride in the solution suppresses the formation of hypochlorous acid.

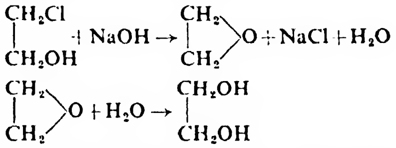
(2) Hydrolysis of ethylene dichloride by water alone under pressure, by aqueous sodium carbonate [53, 1917], or under other slightly modified conditions.

(3) Hydrolysis of ethylene chlorohydrin by heating under pressure with aqueous sodium carbonate or bicarbonate as described by the Société Anonyme d'Explosifs [63, 1913].



$$\begin{array}{l} \mathrm{CH_2Cl} \\ | \\ \mathrm{CH_2OH} \end{array} + x\mathrm{H_2O} + \mathrm{NaHCO_3} \rightarrow \begin{array}{l} \mathrm{CH_2OH} \\ | \\ \mathrm{CH_2OH} \end{array} + \mathrm{NaCl} + x\mathrm{H_2O} + \mathrm{CO_2}$$

(4) Conversion of chlorohydrins to alkylene oxides by lime or caustic alkali and hydrolysis of the oxides by water or very dilute acid, as first described by Henry [39, 1907].



$$\begin{array}{l} \mathrm{CH_2Cl} \\ | \\ \mathrm{CH_2OH} \end{array} + \mathrm{NaOH} \rightarrow \begin{array}{l} \mathrm{CH_2} \\ | \\ \mathrm{CH_2} \end{array}\!\!>\mathrm{O} + \mathrm{NaCl} + \mathrm{H_2O}$$

$$\begin{array}{l} \mathrm{CH_2} \\ | \\ \mathrm{CH_2} \end{array}\!\!>\mathrm{O} + \mathrm{H_2O} \rightarrow \begin{array}{l} \mathrm{CH_2OH} \\ | \\ \mathrm{CH_2OH} \end{array}$$

(5) The direct catalytic oxidation of ethylene to ethylene oxide absorbing and hydrolysing the oxide in cold acidulated water is also of great interest.

Since the chemistry involved in these processes is very simple and has long been known, most of the patents which have been issued in recent years are for very specific process improvements. In this brief discussion no attempt is made to distinguish between similar patents or to mention all of them. The same considerations apply equally to the related derivatives, many of which are now of commercial importance.

Intermediate Products

Olefine Dihalides.

Dichlorides made by the addition of chlorine to olefines are of little or no importance as raw materials for the manufacture of glycols, with the exception of ethylene dichloride. In early investigations both ethylene dichloride and dibromide were used. Ethylene dichloride is obtained as one of the products of the reaction of ethylene and chlorine water. Gomberg [36, 1919] noted that when the final concentration of ethylene chlorohydrin had reached 130 g. per litre the ethylene distribution was 85% of the chlorohydrin and 15% of the dichloride. The addition of chlorine to ethylene is slow in the absence of catalysts or solvents. Substitution usually takes place forming trichloroethane and other high-boiling products. Good yields of dichloride are favoured by low temperatures [7, 1917; 3, 1930] and Curme [22, 1919] has described its production by passing ethylene, under pressure, into liquid chlorine below 0° C.

Wurtz first made ethylene glycol, in 1857, from ethylene dibromide by heating with anhydrous sodium acetate and hydrolysing the diacetate [69, 1857]. The first process of industrial interest was that of Matter, noted above.

Matter's process is carried out by heating ethylene dichloride with aqueous sodium carbonate at 130 to 140°, in an autoclave under moderate pressures. The reaction is slow, requiring about 6 hours, and the separation of much salt in concentrating the glycol is very troublesome. Difficulties connected with the separation of salt are also encountered when the chlorohydrin is hydrolysed with soda. The hydrolysis of the chlorohydrin is, however, much more rapid and the soda required and the resulting salt is only half as great as in the Matter process. These difficulties are largely avoided when ethylene oxide is the intermediate substance.

The conversion of other alkylene dichlorides to glycols in general gives poorer yields, although Matter states that his method also gives good yields of propylene glycol from propylene dichloride. Bainbridge [4, 1914] confirmed earlier work that ethylene dibromide gives nearly theoretical yields of glycol diacetate by heating with potassium acetate but that propylene dibromide gives about $\frac{2}{3}$ bromopropylene $CH_3CH = CH_2Br$ and $\frac{1}{3}$ glycol diacetate. A process very similar to Matter's was patented by Hibbert [41, 1917].

Much of the early experimental work in this field was carried out on the dihalides. While none of this work resulted in anything of industrial interest, much of it is of interest in understanding the chemistry of these substances. Atkinson [1, 1858] made ethylene glycol by heating ethylene dibromide with potassium acetate in 85% alcohol. He stated that the dichloride can be used in the same way but requires heating at 100° C. for 3 or 4 days. Atkinson obtained glycol mono-acetate which was saponified to the glycol. The method of Atkinson was further studied by Demole [26, 1874], and Erlenmeyer [31, 1878] reported a yield of 65% of the theory by this method. L. Henry and P. Henry [40, 1896] showed that good yields of glycol could be obtained by heating ethylene dibromide with dry sodium acetate in 90% methyl alcohol, glycol diacetate being formed readily at 100 to 105°, this being converted to glycol and methyl acetate. Similarly ethylene dichloride gives good yields of glycol by heating with sodium formate in methyl alcohol at about 165° C. [11, 1917]. In view of the interest in vinyl compounds it may be noted that ethylene dibromide heated with aqueous potassium carbonate gives mainly glycol and a small yield of vinyl bromide, $CH_2 = CHBr$, but alcoholic caustic soda yields exclusively vinyl bromide [6, 1933].

Some interest has been shown in the hydrolysis of ethylene dichloride by heating with water under pressure. Carius [15, 1864] reported that the hydrolysis of ethylene dibromide, by heating with water under pressure, gave poor yields of glycol due to decomposition of glycol by the acid formed. Niederist [56, 1879] reported a yield of 60% of the theory by this method. Hough [42, 1916], who was one of the pioneers in the use of glycol dinitrate in dynamite, proposed to catalyse the hydrolysis by heating ethylene dichloride with water and ferric oxide under pressure.

On account of the importance of ethylene dichloride, $CH_2Cl \cdot CH_2Cl$, as a solvent the following physical properties are noted: boiling-point 83·5° C. at 760 mm.; freezing-point −36° C.; d_4^{20} 1·2569; specific heat at 30° C. 0·3054 calories per gram; latent heat of evaporation 77·34 calories per gram at 82·2° C. It is miscible with essential oils, fatty oils, and petroleum oils. Paraffin wax is only very sparingly soluble in this solvent below 25° C., and this property has been utilized in the dewaxing of petroleum distillates [52, 1932] and for the separation of waxes from crude petroleum [38, 1935]. It is slightly inflammable and is sometimes blended with 25% by volume of carbon tetrachloride to overcome this hazard. It is more stable to water and steam than carbon tetrachloride. Its properties as a solvent and as a component of solvent mixtures have been reported by Fife and Reid [33, 1930].

Several industrial chemical uses of ethylene dichloride have been developed, of which the manufacture of ethylene diamine [23, 1932] by reaction with ammonia, and the manufacture of rubber-like material by its reaction with alkali polysulphides may be mentioned.

Ethylene dibromide was formerly used for the laboratory preparation of ethylene glycol. It is manufactured on a large scale for use in Ethyl Fluid with tetra-ethyl lead.

Propylene dichloride has not been manufactured on a very large scale and has found no important industrial application. The corresponding propylene glycol, $CH_3CHOH \cdot CH_2OH$, is not as satisfactory as ethylene glycol for most of the industrial uses in which the latter is used. Propylene glycol is much more easily made from the chlorohydrin or from propylene oxide than from the dichloride. Essex and Ward [32, 1923] state that good yields of allyl chloride are obtained by decomposing propylene dichloride by passing over a catalyst containing calcium chloride at 300 to 350° C. Decomposition of propylene dichloride with caustic alkali yields no allyl chloride but a mixture of 1-chloropropylene and 2-chloropropylene [37, 1927]. Allyl chloride, if produced in quantity by the method of Essex and Ward, would make possible the industrial synthesis of glycerol. At present the only industrial source of allyl compounds, allyl alcohol, is in the products of wood distillation. Allyl chloride or bromide is of considerable interest for the laboratory synthesis of hydrocarbons containing a double bond on the two end carbon atoms, as, for example, normal hexene-1 [12, 1918].

Chlorohydrins.

The first preparation of ethylene chlorohydrin by the addition of hypochlorous acid to ethylene was described by Carius in 1862 [14, 1862]. It is curious that the method of making dilute hypochlorous acid solutions first described by Williamson in 1845 [67, 1845] and also given in Gmelin's well-known *Handbook of Chemistry* in 1849 should have been the best and most convenient source of hypochlorous acid for preparing chlorohydrins until 1919 when Gomberg published his results on the use of chlorine water for this purpose. Williamson's method consisted in passing chlorine into a cold aqueous alkali carbonate solution, forming CO_2, alkali chloride and free hypochlorous acid. This is essentially the same method of preparing hypochlorous acid solutions as that recommended by Wohl and Schweitzer much later [68, 1907]. In this connexion it may be noted that it was shown as early as 1878 that ethylene chlorohydrin is practically not affected by excess hypochlorous acid or chlorine [58, 1878]. H. V. Walker made hypochlorous acid, for the production of amylene chlorohydrins, by treating aqueous sodium hypochlorite with an excess of sodium bicarbonate. Essex and Ward (loc. cit.) passed ethylene and carbon dioxide into sodium hypochlorite, and during the World War ethylene chlorohydrin was manufactured in Germany by passing ethylene and carbon dioxide into aqueous solutions of bleaching powder [57, 1919]. Ethylene and propylene chlorohydrins were made on a small commercial scale in 1918 by using

Williamson's method of making hypochlorous acid and continuously circulating the cold dilute solution through a tower in contact with purified oil gas under pressure [8, 1923; 10, 1923; 9, 1920].

Curme and Young [24, 1923] described liberating hypochlorous acid from sodium hypochlorite by adding excess chlorine, a method long known, but the patent specifies adding insufficient chlorine to liberate all of the hypochlorous acid. Such mixtures are notoriously unstable and this procedure was corrected in the method proposed by Young [73, 1923] who continuously added a small proportion of sodium hypochlorite to a circulating body of solution to which chlorine was also added. The method of Gomberg is more efficient and avoids the use of soda or alkali.

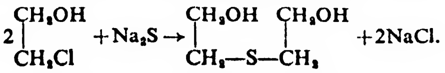
Since the chlorohydrins readily hydrolyse, distillation equipment for concentrating chlorohydrins must be capable of withstanding the action of hot dilute hydrochloric acid. Special stoneware towers or packed towers lined with acid-proof brick are suitable for this purpose. In this way dilute chlorohydrin solutions are readily concentrated to the azeotropic mixture of ethylene chlorohydrin and water, containing 42·5% chlorohydrin and boiling at 95·8° C., at 735 mm.

For the conversion of ethylene chlorohydrin to glycol, either through the intermediate formation of ethylene oxide or by hydrolysis with aqueous sodium carbonate, it is not necessary to separate anhydrous chlorohydrin. If the dilute chlorohydrin is concentrated in a stripping tower the hot vapours may be passed into a scrubbing tower containing hot milk of lime or caustic alkali to produce ethylene oxide which passes overhead and may be condensed or absorbed in cold 1% sulphuric acid for conversion into glycol.

Anhydrous ethylene chlorohydrin distills at 132° C. at 761 mm. and has the density, d_4^{20}, 1·1980. Anhydrous ethylene and propylene chlorohydrins can most conveniently be made from the azeotropic products by salting out in the presence of benzene and distilling the latter.

Although anhydrous ethylene chlorohydrin is an excellent solvent for cellulose acetate and many resins, the ease with which it hydrolyses, liberating hydrochloric acid, has prevented its use in lacquer solvent compositions. The chemical reactivity of chlorohydrins of this type is evidently due to the proximity of the chlorine and hydroxyl group, since in chlorohydrins in which these groups are separated by one or more CH_2 groups the reactivity of the chlorine atom is substantially that of the alkyl chlorides.

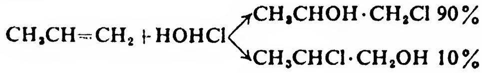
The hydrolysis of ethylene chlorohydrin by water alone yields acetaldehyde and ethylene glycol [49, 1902]. Caustic alkalis give nearly quantitative yields of ethylene oxide under conditions permitting the removal of the oxide as fast as formed, caustic alkalis reacting with the oxide in solution to form gummy condensation or polymerization products. Sodium sulphide in aqueous solution readily gives good yields of beta-thio-diglycol [54, 1887].



$$2\begin{array}{l}CH_2OH\\ |\\ CH_2Cl\end{array} + Na_2S \rightarrow \begin{array}{l}CH_2OH\\ |\\ CH_2\end{array}\!\!-\!S\!-\!\!\begin{array}{l}CH_2OH\\ |\\ CH_2\end{array} + 2NaCl.$$

Potassium cyanide in alcohol solution readily gives the cyanohydrine which on treating with concentrated hydrochloric acid yields chloropropionic acid [46, 1917]. Concentrated sulphuric acid on anhydrous ethylene chlorohydrin [47, 1921] gives a good yield of BB′-dichlorodiethyl ether, a solvent known commercially as Chlorex and used in the petroleum industry as one of the solvents in the solvent refining of lubricating oils. This solvent, boiling at 178° C., is relatively stable. With alcohol it becomes a solvent for cellulose esters [33, 1930]. Ethylene chlorohydrin has had many applications in organic synthesis which cannot be reviewed here. It is commonly supplied in the form of 42% aqueous solution.

Propylene also reacts readily with hypochlorous acid to give a mixture of the two isomeric chlorohydrins [62, 1918].



$$CH_3CH{=}CH_2 + HOHCl \begin{array}{l}\nearrow CH_3CHOH\cdot CH_2Cl\ 90\%\\ \searrow CH_3CHCl\cdot CH_2OH\ 10\%\end{array}$$

Among the higher ethylene homologues the chlorine water method gives greater proportions of dichlorides. As noted above, Walker [66, 1910] made amylene chlorohydrins by treating with cold aqueous solutions of hypochlorous acid made by the action of sodium bicarbonate on sodium hypochlorite.

The action of hypochlorous acid on the higher ethylene homologues, cracked petroleum olefines, terpenes, &c., has been studied very little. A convenient reagent for making chlorohydrins, for research purposes, is that of Detoeuf [27, 1922] who uses *N*-chloro-urea as a source of hypochlorous acid. The yields of chlorohydrins are generally good, 50 to 75% of the theory, though the reaction is slow. Detoeuf in this way made the chlorohydrins of trimethyl ethylene, hexene-2, tetramethyl ethylene, isoheptene-1, octene-2, styrene, cyclohexene, &c.

The properties of some of the simpler chlorohydrins are as follows:

Substance	*B.p ° C.*	*Density*
$CH_3CHCl\cdot CH_2OH$ . . .	133–4	d_4^{20} 1·103
$CH_3CHOH\cdot CH_2Cl$ . . .	126–7	d_4^{20} 1·111
$CH_3CH_2CHOH\cdot CH_2Cl$ . .	141	..
$CH_3CHOH\cdot CHCl\cdot CH_3$ . .	138–9	d_0^0 1·0868
$(CH_3)_2COH\cdot CH_2Cl$ . . .	128	d_0^0 1·0878
$CH_3CHOH\cdot CHCl\cdot CH_2CH_2CH_3$.	170	d_4^{11} 1·018
Cyclohexene chlorohydrin . .	84–5 (16 mm.)	d_4^0 1·138

Alkylene Oxides.

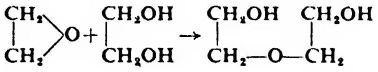
The simpler alkylene oxides are very reactive, being readily hydrolysed to the corresponding glycols, react readily with ammonia to form hydroxy alkyl amines, and undergo a wide variety of reactions of great interest. Ethylene oxide itself has found application as an insecticide and is used for treating grain and for the protection of furs in storage. Their chief importance, however, is as intermediates in the manufacture of glycols, glycol ethers, and hydroxy alkyl amines.

In the manufacture of ethylene glycol ethylene chlorohydrin is converted into the oxide by the use of lime, which is a great saving over the use of soda or caustic alkali, and the troublesome separation of glycol and salt is largely avoided.

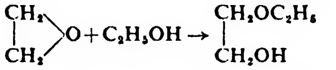
The simpler alkylene oxides have long been known, having been made by the action of caustic alkali on the chlorohydrins [70, 1859]. Walker [66, 1910] used slaked lime for making amylene oxides from the chlorohydrins. Good yields of ethylene and propylene oxides may be obtained by gradually adding caustic alkali [13, 1926] or lime to hot chlorohydrin solutions, the oxides being removed as fast as formed [2, 1920; 17, 1929]. Up to the present time (1935) all of the ethylene and propylene oxides produced industrially have been made from the chlorohydrins.

The direct oxidation of ethylene to ethylene oxide is of great interest as thus the use of chlorine and alkali is avoided. Such a method was suggested by the work of Lenher [51, 1931], who passed oxygen with excess ethylene through a Pyrex tube heated to 535° C. Various catalysts [64, 1931] have been proposed for the reaction [28, 1933]. Francon [34, 1933] reports that the optimum temperature is 375° C. The catalysts used are stated to be poisoned by traces of sulphur compounds. Finely divided silver is one of the catalysts recommended [64, 1931; 5, 1935] and temperatures within the range 350–400° C. A silver catalyst promoted by small quantities of iron, copper, or gold is recommended by Lefort [50, 1935].

The ease with which the simpler alkylene oxides are hydrolysed by dilute acids [39, 1907] to the corresponding glycols is utilized in the manufacture of glycols. Ethylene oxide is converted to glycol by heating with water under pressure, as noted by Wurtz [71, 1860], and isobutylene oxide is rapidly hydrolysed by water alone at ordinary temperatures [30, 1883]. Glycol ethers are also formed if small proportions of water are used, since the more reactive oxides, such as ethylene oxide, react with other glycols or alcohols.



and



The latter reaction is used in making mono-ethers of ethylene and propylene glycols, a series of which is produced commercially.

Oxides of this type tend to rearrange to aldehydes on treatment with dilute acids. Good yields of alkyl ethers are favoured by using anhydrous alcohols in the above reaction. Thus propylene oxide yields propionic aldehyde, and isobutylene oxide yields isobutyric aldehyde. The reaction products, with acidulated alcohols, therefore may contain these aldehydes and their acetals, in addition to the glycol ethers.

The glycol ethers can also be prepared by heating the oxides with alcohols, in autoclaves, to about 150° C. for several hours [72, 1928]. A continuous process for making alcohol and phenol ethers by reaction with ethylene oxide at high temperatures, 130–180° C., has also been described [45, 1929]. The reaction of substances containing one or more hydroxyl groups with ethylene oxide and similar oxides is quite general and has been applied to carbohydrates, cellulose, &c.

The anhydrous chlorohydrins also react with sodium alcoholates to give glycol mono-alkyl ethers [20, 1924].

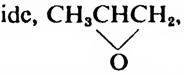
The mono-methyl, -ethyl, -normal butyl, and -amyl ethers of ethylene glycol have been employed in lacquer compositions. Some of the physical properties of the better known ethylene glycol ethers are as follows [25, 1926]:

Mono-alkyl Ethers of Ethylene Glycol

	B.p. ° C. at 743 mm.	D_{15}^{15}	M_D^{26}
Methyl . . .	124·5	0·9748	1·4004
Ethyl . . .	134·8	0·9360	1·4042
Isopropyl . . .	144·0	0·9139	1·4080
n-Propyl . . .	150·0	0·9110	1·4125
Isobutyl . . .	158·8	0·9130	1·4135
n-Butyl . . .	170·6	0·9188	1·4177
Isoamyl . . .	181·0	0·9000	1·4198

The dialkyl ethers of the simple glycols are generally not as valuable as lacquer solvents as the mono-alkyl ethers.

It has been noted above that, in accordance with the general reaction, ethylene oxide reacts with ethylene glycol to form a series of glycol ethers. The simplest one of the series, diethylene glycol, $CH_2OH\ CH_2O\ CH_2\ CH_2OH$, is a very hygroscopic liquid boiling at 244·5° C., and its dinitrate is of value in the manufacture of low-freezing dynamite. The dinitrate is more fluid than nitroglycerol, freezes when pure at −11·3° C., and is less sensitive to shock than nitroglycerol or glycol dinitrate [61, 1913; 43, 1932]. The mono-ethyl ether of diethylene glycol, boiling-point 198° C. at 760 mm., is also a solvent for cellulose nitrate and many gums and resins. The mono-alkyl ethers of diethylene glycol are marketed under the name of Carbitols, and the ethylene glycol mono-alkyl ethers are sold under the series name of Cellosolve.

Propylene oxide,  $CH_3\underset{O}{\underset{\diagdown\diagup}{CHCH_2}}$, a liquid boiling at 35° C. at 760 mm. undergoes the same series of reactions already noted in the case of ethylene oxide. With alcohols a series of mono-alkyl ethers is formed.

Mono-alkyl Ethers of Propylene Glycol

	B.p. ° C. at 743 mm.	D_{15}^{15}	M_D^{20}
Methyl . . .	122·8	0·9335	1·4035
Ethyl . . .	133·0	0·9090	1·4061
Isopropyl . . .	141·5	0·8900	1·4062
n-Propyl . . .	150·0	0·8970	1·4102
Isobutyl . . .	161·3	0·8810	1·4112
n-Butyl . . .	170·6	0·8890	1·4151
Isoamyl . . .	183·3	0·8835	1·4182

Both ethylene oxide and propylene oxide react with aqueous ammonia to form mono-, di-, and tertiary-basic derivatives. The ethanol amines are best known industrially; mixtures of them having been employed to remove carbon dioxide and hydrogen sulphide from various industrial gases (see the article on this subject by R. R. Bottoms, p. 1517). In the preparation of the ethanol amines an excess of ammonia favours the formation of mono-ethanol amine and an excess of ethylene oxide favours the formation of tri-ethanol amine [35, 1933; 48, 1897]. The three ethanol amines are miscible with water. The fatty acid salts are excellent emulsifying agents. Ethanol amine oleate is useful in forming oil-in-water emulsions [65, 1929]. The ethanol amines have been suggested for a wide variety of other industrial applications [29, 1934].

The use of ethylene oxide as a fumigant and insecticide has been referred to. It is not without toxic effects upon human beings, but generally is not considered dangerous in this respect. Exposure to concentrations up to 32 g. per cu. metre for a short time are reported not dangerous [55, 1932]. To reduce the fire hazard in the use of the vapour mixed with air the admixture of about 7 lb. of carbon dioxide to 1 lb. of ethylene oxide is recommended. A concentration of 2 lb. of ethylene oxide in 1,000 cu. ft. of air space is reported to be 100% fatal to insects in grain, solid foods, fur, clothing, &c., in 24 hours [19, 1928; 44, 1928].

The Glycols.

The glycols which may be made from the olefines of oil gas include ethylene glycol, propylene glycol, and butylene glycols (butane-1,2-diol and butane-2,3-diol and possibly isobutylene glycol). The higher ethylene glycol homologues have aroused little or no industrial interest and little research has been carried out on them as compared with ethylene and propylene glycols and their derivatives. 1,3-butylene glycol has been suggested as an intermediate for the manufacture of butadiene, but this glycol has not been made from oil gas butene. By making the chlorohydrins of oil gas butenes both the 1,2- and 2,3-butene glycols would result.

The intermediate products produced in converting ethylene and propylene into the corresponding glycols have been discussed in the foregoing discussion. The advantage in making these glycols from the oxides rather than by heating the chlorohydrins with alkali carbonate solutions has also been noted. The commercial disposition of the by-product polyglycols, obtained by hydrolysing ethylene oxide, has apparently been largely solved by the use of di-ethylene glycol in the form of the dinitrate in low-freezing dynamite, one of the first industrial applications of ethylene glycol itself.

Up to the present time industrial practice has been practically limited to the production of the ethylene series, the propylene in the oil gas being converted to isopropyl alcohol, acetone, ketene, and acetic anhydride.

Ethylene glycol boils at 197·5° C. at 760 mm. and has a density of 1·115 at 20° C. The toxic properties of ethylene glycol have been reviewed by Ellis [29, 1934]. The largest use of ethylene glycol, in the United States, is as an anti-freeze solution for automobile radiators. Mixtures containing 60 to 65 parts of water and 35 to 40 parts of the glycol are commonly used; an aqueous mixture containing 60% ethylene glycol, by volume, freezes at $-4°$ C. ($-56°$ F.).

Another important use of ethylene glycol is in the form of the dinitrate, a component of low-freezing nitroglycerol dynamite. The dinitrate has long been known. Conditions for its nitration have been given by Rinkenbach [60, 1926], who gives its properties as follows: d^{0}_{15} 1·5176, d^{15}_{15} 1·4962, freezing-point $-22{\cdot}3°$ C., vapour pressure at 22° C., 0·0565 mm. Its mixture with nitroglycerol in dynamite has been described by Matthews, Strange, and Bliss [16, 1931], by Hough [42, 1916], and others. The physiological properties of the dinitrate are similar to those of nitro-glycerol.

The glycol esters of dicarboxylic acids are of interest, these products being highly polymerized. Though having very high molecular weights most of them are microcrystalline solids [16, 1931].

Up to the present time the olefine raw materials used for the manufacture of glycols, alcohols, and other chemical products have been derived from cracking gas oil under high temperature—low-pressure or vapour-phase conditions, and as by-products of pressure cracking for gasoline. Chemical manufacturers mainly interested in the manufacture of chemical products have been active in developing cracking conditions to produce a maximum of the simple olefines from fuel oils and gas oils, together with a minimum of such products as gasoline or motor fuel. It is possible that developments along these lines will proceed rapidly quite independently of the work being done by oil-refining companies in the utilization of refinery by-products.

Chemical manufacturers are also actively interested in new efforts to produce benzene, naphthalene, and other aromatic hydrocarbons from petroleum; and the simple olefines are also produced incidental to cracking operations of this type. A still more promising source of the simple olefines in large quantities is in the cracking of light hydrocarbons such as butane and propane from refinery gas and natural gas. It is at present not possible to incorporate all of the butane, produced in refinery operations, in motor fuel. Propane is normally entirely excluded and is commonly rated only at gas fuel value. The large quantities of propane and butane available in connexion with gasoline recovery from natural gas are actively sought as raw material for the production of gasoline by high temperature cracking and polymerization. Large quantities of gas rich in olefines are at least potentially available in operations of this kind. The manufacture on a large scale of such organic chemicals as the glycols and related compounds, alcohols, ketones, acetic acid, acetic anhydride, chlorinated solvents such as ethylene dichloride, trichloro-ethylene, ethyl chloride, olefine oxides, and other organic chemicals derived from these basic organic chemicals may be expected to increase markedly within the next few years.

REFERENCES

1. Atkinson, E. *Phil. Mag.* (4), **16**, 433 (1858).
2. Badische A. and S. Fabr. G.P. 299,682 (1920).
3. Bahr, H., and Zieler, H. *Z. angew. Chem.* **43**, 233 (1930).
4. Bainbridge, E. G. *J.C.S.* **105**, 2291 (1914).
5. Bataafsche Petroleum Maatsch. B.P. 434,011 (1935).
6. Bernoulli, A. L., and Kambli, W. *Helv. Chim. Acta*, **16**, 1187 (1933).
7. Brooks, B. T. *Ind. Eng. Chem.* **9**, 750 (1917); U.S.P. 1,231,123 (1915).
8. —— U.S.P. 1,465,595 (1923); 1,394,664, 1,498,781, 1,498,782.
9. —— *Chem. Met. Eng.* **22**, 629 (1920).
10. Brooks, B. T., and Eldred, B. E. U.S.P. 1,465,601 (1923).
11. Brooks, B. T., and Humphrey, I. W. U.S.P. 1,215,903 (1917).
12. —— —— *J.A.C.S.* **40**, 822 (1918).
13. Burdick, J. N. U.S.P. 1,589,358 (1926); 1,589,359 (1926).
14. Carius, L. *Ann.* **124**, 266 (1862); **126**, 197 (1863).
15. —— *Ann.* **131**, 172 (1864).
16. Carothers, W. *Chem. Reviews*, **8**, 361 (1931).
17. Chemische Fabr. Kalk. G.P. 403,643 (1929).
18. Claude, G. B.P. 223,489 (1929).
19. Cotton, R. T., and Roark, R. C. *Ind. Eng. Chem.* **20**, 805 (1928); U.S.P. 1,791,429 (1931): assigned to the Government and People of the U.S.A.
20. Cretcher, L. H., and Pittenger, W. H. *J.A.C.S.* **46**, 1503 (1924).
21. Curme, G. U.S.P. 1,422,182, 1,422,183, 1,422,184 (1922).
22. —— U.S.P. 1,315,542, 1,315,545 (1919).
23. —— U.S.P. 1,832,534 (1932).
24. Curme, G., and Young, C. O. U.S.P. 1,456,916 (1923).
25. Davidson, J. G. *Ind. Eng. Chem.* **18**, 669 (1926).
26. Demole, E. *Ber.* **7**, 641 (1874); *Ann.* **173**, 117 (1874).
27. Detoeuf, A. *Bull. Soc. Chim.* **31**, 102,169 (1922).
28. du Pont, E. I. de Nemours Co. B.P. 400,297 (1933).
29. Ellis, C. *The Chemistry of Petroleum Derivatives*, 553 (Chemical Catalog Co. New York, 1934).
30. Eltekow, A. *Ber.* **16**, Ref. 395 (1883).
31. Erlenmeyer, E. *Ann.* **192**, 244 (1878).
32. Essex, H., and Ward, A. L. U.S.P. 1,477,047 (1923).
33. Fife, H. R., and Reid, E. W. *Ind. Eng. Chem.* **22**, 513 (1930).
34. Francon, J. *Chim. et Ind.*, Special No., June 1933, 869.
35. Germann, F. E. E., and Knight, O. S. *J.A.C.S.* **55**, 4150 (1933).
36. Gomberg, M. *J.A.C.S.* **41**, 1414 (1919).
37. Goudet, H., and Schenker, F. *Helv. Chim. Acta*, **10**, 132 (1927).
38. Henderson, L. M., Ferris, S. W., and Cowles, H. C. U.S.P. 1,991,389 (1935).
39. Henry, L. *Compt. rend.* **144**, 1404 (1907).
40. Henry, L., and Henry, P. *Bull. Belg. Acad.* **32**, 402 (1896); **42**, 732 (1906).
41. Hibbert, H. U.S.P. 1,270,759 (1917).

42. Hough, A. U.S.P. 1,206,222 (1916).
43. —— C.P. 325,098 (1932).
44. Hoyt, L. F. *Ind. Eng. Chem.* **20**, 835 (1928).
45. I.G. Farbenindustrie A. G. B.P. 342,022 (1929).
46. Jacobs, W. A., and Heidelberger, M. *J.A.C.S.* **39**, 1465 (1917).
47. Kamm, O., and Waldo, J. H. *J.A.C.S.* **43**, 2223 (1921).
48. Knorr, L. *Ber.* **30**, 909 (1897).
49. Krassuski, K. *Chem. Centr.* 1902 (2) 19.
50. Lefort, T. E. U.S.P. 1,998,878 (1935).
51. Lenher, S. *J.A.C.S.* **53**, 3737 (1931); **54**, 1830 (1932).
52. Livingston, C. J. U.S.P. 1,848,636 (1932).
53. Matter, O. U.S.P. 1,237,076 (1917); G.P. 299,074 (1920); 369,502 (1924); 373,187 (1924).
54. Meyer, V. *Ber.* **19**, 3259 (1887).
55. Müller, A. *Chem. Abs.* **26**, 1063 (1932).
56. Niederist, G. *Ann.* **196**, 354 (1879).
57. Norris, C. F. *Ind. Eng. Chem.* **11**, 817 (1919).
58. Pebal, L. *Ber.* **11**, 2188 (1878).
59. Prileschajew, N. *Ber.* **42**, 4811 (1909); *Chem. Zentr.* **1912 (2)**, 2090.
60. Rinkenbach, W. H. *Ind. Eng. Chem.* **18**, 1195 (1926).
61. Rinkenbach, W. H., and Aarousen, H. A. *Ind. Eng. Chem.* **23**, 160 (1931).
62. Smith, L. *Z. physik. Chem.* **93**, 59 (1918).
63. Soc. Anon. d'Explosifs. F.P. 458,733 (1913).
64. Soc. française de catalyse generalisée. F.P. 739,562 (1931); 41,811 (1933), addition to 739,562.
65. Trusler, R. B. *Ind. Eng. Chem.* **21**, 685 (1929).
66. Walker, H. V. U.S.P. 972,952 (1910).
67. Williamson, A. W. *Ann.* **54**, 140 (1845).
68. Wohl, A., and Schweitzer, H. *Ber.* **40**, 94 (1907).
69. Wurtz, A. *Ann.* **104**, 174 (1857).
70. —— *Ann.* **110**, 125 (1859); *Ann. Chim.* 1863 (3), **69**, 317.
71. —— *Ann.* **113**, 255 (1860).
72. Young, C. O. U.S.P. 1,696,874 (1928).
73. —— U.S.P. 1,456,959 (1923).

SELECTED BIBLIOGRAPHY

Ellis, C. *The Chemistry of Petroleum Derivatives*, 1152 pp. (The Chemical Catalog Co. New York, 1934).

Gersdorff. *A Bibliography of Ethylene Dichloride.* U.S. Dept. of Agriculture, Misc. Publ. No. 117 (1932).

Lawrie, J. W. *Glycerol and the Glycols.* Amer. Chem. Soc. Monograph Series. Chem. Catalog Co. New York, 1928.

Zinakov. *J. Chem. Ind.* (Moscow), No. 6, 36 (1932). Ethylene Dichloride.

THE CHLORINATION OF METHANE AND ITS HOMOLOGUES

By Professor H. B. HASS, Ph.D.
Head, Department of Chemistry, Purdue University

Introduction

ALL the members of the methane series of hydrocarbons undergo substitution reactions with the halogens. In the case of iodine, the reaction

$$C_nH_{2n+2}+X_2 \rightarrow C_nH_{2n+1}X+HX$$

is reversible, so that significant yields of iodides can be obtained only in the presence of a reagent such as iodic acid, which removes the hydriodic acid as it is produced. Bromination takes place readily under the influence of light and/or high temperatures but is not of technical importance at present. Fluorinations have been relatively little studied and are apparently difficult to control because of the violence of the reaction. On the other hand, the reaction of chlorine with hydrocarbons of the methane series has been widely investigated, especially with a view towards its industrial utilization. The principal factors which caused the performance of these researches are (1) the great abundance and cheapness of the simpler paraffin hydrocarbons, especially since the relatively recent application of efficient rectification apparatus to natural gas gasoline, (2) the small number of the modes of chemical attack to which saturated hydrocarbons are susceptible, (3) the established markets for certain of their chlorinated derivatives, and (4) the availability of unlimited quantities of cheap chlorine produced by the electrolytic alkali and magnesium industries. As a result, several successful commercial installations have utilized these reactions as the starting-point for a number of interesting syntheses.

Difficulties met with in the Chlorination of the Paraffins

Before discussing in detail the course of the chlorination reaction, it may be desirable to call attention to the difficulties which must be overcome before this substitution can be carried out; one is thus led to a more ready appreciation of the devices which have been used to surmount these obstacles.

(1) The reaction is a highly exothermic one. Jones, Allison, and Meighan [32, 1921] quote data from which have been obtained the following approximate figures for the heats of reaction of methane and its chlorinated derivatives at 400° C. in gaseous phase:

$$CH_4+Cl_2 \rightarrow CH_3Cl+HCl+33 \text{ cal.}$$
$$CH_3Cl+Cl_2 \rightarrow CH_2Cl_2+HCl+27 \text{ cal.}$$
$$CH_2Cl_2+Cl_2 \rightarrow CH_3Cl+HCl+34 \text{ cal.}$$
$$CHCl_3+Cl_2 \rightarrow CCl_4+HCl+43 \text{ cal.}$$

While these figures are based upon somewhat unreliable thermal data, it is apparent that about 30–35 cal. per mole of chlorine reacting must be taken care of in the chlorination of a paraffin. Incidentally, these data furnish another illustration of the absence of a parallelism between reaction rates and reaction heats. Pease and Walz [43, 1931] have shown that methyl chloride chlorinates at about twice the rate of methane, although the heat of reaction is appreciably less.

Under conditions of too high concentration of chlorine and/or excessive temperatures, another type of reaction sets in, represented by the following equation:

$$CH_4+2Cl_2 \rightarrow C+4HCl+67{\cdot}8 \text{ cal.}$$

In the chlorination of the homologues of methane, excessive temperatures give rise to the formation of olefines. These olefines are probably formed by reactions of the type:

$$C_nH_{2n+1}Cl \rightarrow C_nH_{2n}+HCl.$$

Since the olefines thus formed have boiling-points rather close to those of the paraffins used as starting material, they are recycled with the unreacted hydrocarbon and are thus converted to dichlorides and chloro-olefines.

$$C_nH_{2n}+Cl_2 \rightarrow C_nH_{2n}Cl_2$$
$$C_nH_{2n}+Cl_2 \rightarrow C_nH_{2n-1}Cl+HCl.$$

The saturation of an olefine double bond with chlorine leads also to an appreciable formation of trichlorides and more highly chlorinated material.

A still further difficulty introduced by the exothermic nature of the reaction is the danger of explosion. It has been repeatedly observed that very violent and even dangerous explosions can be produced by reaction between chlorine and saturated hydrocarbons.

(2) The partially chlorinated derivatives are capable of being chlorinated further so that it is impossible to stop the reaction sharply at any given point. Thus by-products are obtained which are frequently more or less difficultly utilizable as, for example, the 'amylene dichlorides' formed in the Sharples Solvents Corporation [2, 1929], chlorination of pentanes.

(3) All of the hydrogen atoms present in a paraffin hydrocarbon will be substituted (though not, as a rule, at the same rate) so that mixtures of isomeric chlorides are always obtained except in those cases where all positions are equivalent such as methane, ethane, and neopentane. Usually the different isomers possess different economic values; for the production of alcohols and chlorinated solvents the primary chlorides are generally most valuable. Primary chlorides not only resist thermal decomposition and hydrolysis by water to a greater extent than the secondary and particularly the tertiary isomers, but are usually convertible to alcohols in better yields. The primary alcohols form esters with greater solvent powers for nitrocellulose (higher dilution ratios) than those derived from the secondary isomers and hence are more valuable. A process which would yield exclusively primary chlorides with no formation of olefines or polychlorides would be ideal, but has so far not been devised.

(4) The corrosive nature of chlorine and of hydrochloric acid have introduced engineering difficulties which have only rather recently been overcome.

(5) There is in some cases appreciable difficulty in causing the reaction to go to completion so as to prevent free chlorine from appearing in the gases leaving the chlorinator. This is particularly a problem with methane, both because it chlorinates at a slower rate than its homologues, and because in the chlorination of the homologues the

olefine formation referred to above tends to remove traces of chlorine which may occur in the reaction products.

Means which have been adopted for overcoming the above Difficulties

Jones, Allison, and Meighan [32, 1921] were able to avoid explosions when using mixtures of methane and chlorine well within the explosive limits by passing the gaseous mixture into the heated reaction zone very slowly. This procedure is probably not applicable technically because of the hazard of the presence of considerable quantities of such mixtures.

Experiments have shown that the lower explosive limit of chlorine in hydrocarbon occurs in the case of propane and the butanes at approximately the point where there is one chlorine atom present for each carbon atom. Explosions have been completely avoided by using a concentration of hydrocarbons greater than this. In the industrial processes of Lacy [35], of Ayres [2, 1929; 3], and of Curme [16, 1922] the same means is employed. The use of inert diluents has also been advocated in order to temper the violence of the reaction, e.g. Pfeifer, Mauthner, and Reitlinger [44, 1919], and later, Boswell and McLaughlin [8, 1929] used nitrogen. While in certain cases, where there is no possibility of over-chlorination, such as the chlorination of methane to carbon tetrachloride, it may be advantageous to use foreign diluents, in general it may be said that the best diluent is an excess of the material to be chlorinated. By using an excess of hydrocarbon or of insufficiently chlorinated hydrocarbon, one not only avoids the necessity of separating a foreign diluent from the reaction products but the formation of too highly chlorinated material is minimized. The yield of over-chlorinated material can be suppressed to any desired degree if only a small percentage of the material to be chlorinated is allowed to react at each pass through the chlorinator.

An economic balance must be struck between the advantages of the higher yields of monochlorides which are caused by the lower chlorine concentrations in the reacting hydrocarbon and the increased cost of additional recycling. When chlorination is achieved thermally, recycling involves the expense of heating and cooling large volumes of hydrocarbons. In the case of the further thermal chlorination of the homologous alkyl chlorides, too many passes through the hot reactor may increase the amount of pyrolysis unduly so that too much recycling is undesirable from this standpoint also. The situation is further complicated, when using apparatus of ordinary steel, by the formation of a carbonaceous tar which is capable of plugging small tubes such as are usually employed in heat exchangers. Even when using 3-in. steel pipes it is necessary to suspend operations at intervals and clean them out [45]. Tar formation renders the use of small tubes impracticable, while rapid cooling of the reacted gases is very desirable as a means of diminishing pyrolysis. The procedure employed in the Sharples Solvents Corporation [2, 1929; 3] process for the chlorination of pentanes involves heating the pipes of the chlorinator by a natural gas flame and cooling the reacted gases by means of a condenser composed of relatively large pipes over which cooling water is sprayed. The open type of condenser is preferred because of the ease of detection and repair of leaks which might otherwise result disastrously by introducing hydrochloric acid into the cooling water of the plant.

Elsewhere the fuel economy incident to the use of a heat exchanger has been achieved by employing KA2 chromium-nickel steel in the reactor. This alloy is much less of a catalyst [53] than ordinary steel for the production of olefines and tar, and permits the use of small tubing.

The use of catalysts or of actinic light lowers the necessary reaction temperature—in fact photochemical chlorination of these hydrocarbons can readily be obtained at −80° C.—and thus diminishes the heat requirement of the recycling. According to Ayres [2, 1929], catalysts generally have the effect of increasing the yield of secondary and of tertiary isomers at the expense of the primary chlorides which are usually more desirable. Low-temperature chlorination achieved photochemically also has this effect. Obviously, this does not occur in the chlorination of methane where no isomers are possible. As already pointed out, methane chlorinates more sluggishly than its homologues, so that the use of catalysts is more imperative in this case.

Even when operating at high hydrocarbon-chlorine ratios there is danger of ignition at the point at which chlorine is introduced to the hydrocarbon stream, where its concentration is very high. Large quantities of soot may thus form which soon plug the apparatus and result in failure of the process. Lacy [35] avoided this difficulty by preheating 10 volumes of methane to 370° C., which is considerably above the temperature at which reaction begins, and mixing this with a cold, preformed mixture of 5 volumes of methane and 1 of chlorine. This procedure also renders the process self-supporting thermally and thus makes possible the use of a reactor lined with silica brick and avoids the necessity of contacting the chlorine or chlorides with heated metals. Ayres [2, 1929; 3] pointed out that ignition is impossible at the point of entry of the chlorine if the velocity of the entering chlorine stream is in the neighbourhood of a mile per minute and if both chlorine and hydrocarbon are at comparatively low temperatures. Lunt [36, 1932] recommends a pressure drop of 1·4 to 2·4 atm. at the point of introducing both pentane vapour and chlorine to a common mixing chamber. This would result in jet velocities considerably above those used by Ayres. McBee, working in this laboratory, has found it possible to introduce chlorine even into very hot hydrocarbon vapour (above 600° C.) without soot formation by using a jet through which the chlorine flows at velocities of the order of 50–100 miles per minute.

The formation of olefines occurs to a greater or less extent in any chlorination of methane homologues, thermal, catalytic, or photochemical, which takes place at temperatures above those at which the chlorides decompose. The tertiary chlorides are the worst offenders in this respect, while the primary isomers are most stable. Many chlorination catalysts promote the loss of hydrogen chloride from the mono- and polychlorides; iron, for instance, has this effect. In order to diminish this pyrolysis it is necessary to prevent even momentary excessive temperatures—and here again dilution with an excess of material to be chlorinated plays an important role—and to cool the products of the reaction as quickly as possible. A study of the pyrolysis of 1-chlorobutane and of 2-chlorobutane by Weston and Hass [57, 1932] at 200–700° C. showed much lower pyrolysis rates than those observed in the chlorination of butane within the same temperature range by Hass and McBee [27, 1934]. This fact finds an explanation in the exothermic nature of the chlorination reaction which probably results in the formation of free radicals.

The often-observed inhibition of chlorination reactions

[37, 1906] in the presence of free oxygen was interpreted by Pease and Walz [43, 1931] to indicate a chain mechanism. By analogy with the hydrogen-chlorine reaction one may postulate the following mechanism:

$$\begin{aligned}&(1)\quad Cl_2 \rightleftharpoons 2Cl\\&(2)\quad RH+Cl \rightarrow R+HCl\\&(3)\quad R+Cl_2 \rightarrow RCl+Cl.\end{aligned}$$

The function of heat, light, or catalysts, according to this theory, would be principally to initiate chains by producing chlorine atoms or free organic radicals. A single quantum of light can, by decomposing a chlorine molecule into two chlorine atoms, initiate a reaction chain which accounts for the chlorination of an indefinitely large number of hydrocarbon molecules. Deanesly [19, 1934] has shown that this reaction may be markedly accelerated, especially in the absence of oxygen, by the presence of a small quantity of olefine in the material being chlorinated substitutively. The unsaturated compound is apparently able to initiate reaction chains when it undergoes addition with chlorine.

According to Pease and Walz [43, 1931], the thermal chlorination of methane is a homogeneous reaction. We have observed, however, that the chlorination of the homologues of methane proceeds very slowly until the glass surface of the reaction vessel is coated with a thin film of carbonaceous deposit. In one experiment chlorine and isobutane were separately preheated to 500° C. and mixed at the centre of a bulb the walls of which were kept at 200° C. so that the carbonaceous deposit did not form. No appreciable chlorination resulted, although exploration with a protected thermocouple and with a thermometer showed a large proportion of the contents of the bulb to be at or above the temperature at which chlorination normally occurs. Perhaps in a thermal chlorination the reaction chains are initiated at the carbonaceous deposit on the wall of the reactor and thereafter proceed homogeneously through the mass of reacting gases. Yuster and Reyerson have recently presented data on the chlorination of propane [60, 1935] which led them to the same conclusion. Since the pyrolysis to form olefines has been shown to be a homogeneous rather than a heterogeneous reaction [57, 1932], this indicates the desirability of a large wall contact surface within the reactor relative to its volume, such as has been used by Curme [16, 1922], Mason and Wheeler [40, 1931], and many others. The effect should be to accelerate the chlorination at a given temperature without accelerating the pyrolysis and thus to permit a reduction of the exposure time and/or of the reaction temperature.

The corrosive effects of chlorine and of hydrogen chloride are most evident in the presence of water and can be largely overcome by keeping the system dry. This procedure has been used by Curme in the chlorination of methane, and by Ayres [2, 1929; 3] in the Sharples Solvents Corporation chlorination of pentanes. Water is appreciably soluble in saturated hydrocarbons and, as would be expected, the addition of hydrogen chloride, with the production of the highly polar hydrochloric acid, diminishes greatly its solubility in the non-polar hydrocarbons. As a result, concentrated hydrochloric acid would be deposited at various places in the plant. Ayres [4, 1931] avoids this difficulty by saturating the pentane with dry hydrogen chloride before it enters the chlorination unit and draining off the lower layer of hydrochloric acid which separates by gravity.

Generalizations concerning the Chlorination of the Homologues of Methane

The following critical survey is made in the hope that it will prove to be of value to other workers in the field.

Rule 1. Carbon skeleton rearrangements do not occur during the chlorination of the simpler paraffins if pyrolysis temperatures are avoided. All of the isomers derivable without such rearrangement are always formed [27*a*, 1935].

Perhaps the only remarkable thing about Rule 1 is that it has been so often contradicted. Schorlemmer [47, 1868–70] obtained only 1-chloropropane in the monochloride fraction resulting from reaction of an equimolar mixture of propane and chlorine at room temperature in sunlight. A more careful repetition of his experiment with the use of modern rectification equipment shows that under these conditions one obtains a ratio of about 60% 2-chloropropane : 40% 1-chloropropane. More recent work by Mason and Wheeler [41, 1931] indicates that both monochlorides are obtained in the thermal chlorination of propane. In rectifying these monochlorides, 2-chloropropane (b.p. 34·7° C.) predominates in the first fraction, while 1-chloropropane (b.p. 46·6° C.) occurs chiefly in the later one. Mason and Wheeler found that 'the first fraction was usually larger than the second, suggesting that more of the *n*- than of the *iso*-compound was formed'. Obviously, if we assume reasonably efficient rectification, exactly the reverse is shown by their results.

Butlerov [10, 1867] reported only tertiary butyl chloride and a dichloride boiling at about 105° C., which was chiefly 1,2-dichloroisobutane, in the photochemical chlorination of isobutane. Apparently there was no primary substitution until after the tertiary hydrogen atom had reacted. Actually, under these conditions one obtains 38% tertiary butyl chloride and 62% isobutyl chloride. Mabery and Hudson [38, 1897] chlorinated nearly pure *n*-butane (b.p. −2 to +2° C.) and report only one monochloride, which boiled 68–69° C. This actually was 2-chlorobutane (b.p. 68·25° C.), but Mabery and Hudson decided that it was 1-chloroisobutane (b.p. 68·85° C.). To credit Mabery and Hudson's identification one must postulate a carbon skeleton rearrangement; let us consider this possibility. Mabery and Hudson's dichloride fraction boiled at 121–122° C. The three dichlorides derivable from isobutyl chloride (or isobutane) have the following boiling-points: 1,1-dichloroisobutane, 105–106° C.; 1,2-, 107° C.; 1,3-, 136·0° C. A suitable mixture of 1,2-dichlorobutane (b.p. 124° C.) and *dl* 2,3-dichlorobutane (b.p. 119·5° C.), both of which are actually formed in the chlorination of *n*-butane and/or 2-chlorobutane, would boil largely at 121–122° C. and thus account for Mabery and Hudson's observation. Their results are thus explicable only in the absence of substantial carbon skeleton rearrangement. Chlorination of butane under Mabery and Hudson's conditions by Weston and by McBee has shown no detectable formation of 1-chloroisobutane.

Whitmore and Fleming [24, 1932] reported the production of 6% of tertiary amyl chloride in the chlorination of neopentane, but soon found this conclusion to be erroneous and corrected it [58, 1933]. The theory of carbon skeleton rearrangement is apparently supported by the work of Aschan [1, 1920] and of Wertyporoch [56, 1933], both of whom chlorinated *n*-pentane and obtained a monochloride fraction boiling at about 97° C. As pointed out by Hass and Weber [29, 1934], Wertyporoch's boiling-points, while somewhat inconclusive, indicate strongly, when interpreted in the light of correct boiling-point data for the pure compounds, that no derivatives of isopentane were present in his chlorides obtained from *n*-pentane. Work by Hass and Weber [27, 1935–6] shows conclusively that no significant amount of carbon skeleton rearrangement occurs in the chlorination of normal- and isopentane.

Let us return now to the question of isomeric monochlorides derivable without carbon skeleton rearrangement. The fact that Aschan [1, 1920] obtained only two fractions in the chlorination of *n*-pentane, although three isomers are possible, has been shown by Weber to be due to the fact that the boiling-point of 2-chloropentane (96·7° C.) is so close to that of 3-chloropentane (97·3° C.). Analysis of this mixture by conversion to the anilides has shown both secondary isomers to be present. Both Aschan [1, 1920] and Wertyporoch [56, 1933] report all four monochlorides derivable from isopentane, but Ayres [2, 1929] and Clark [13, 1930] report that 2-chloro-3-methylbutane is not present in the Sharples Solvents Corporation mixed amyl chlorides. The latter statement really means, however, that the corresponding alcohol (3-methylbutanol-2) has not been isolated from 'Pentasol', since the analyses have been made on the amyl alcohols rather than on the chlorides [45]. It has never been shown that 2-chloro-3-methylbutane yields the corresponding alcohol under the Sharples hydrolysis conditions or that it would survive the rather prolonged contact with the iron tubes in the chlorinator. Weber [55, 1935–6] has shown that this chloride is certainly formed in the chlorination of isopentane even at temperatures much higher than those used by Sharples.

Rule 1 extends to the polychlorides at least in the cases of ethane, propane, butane, and isobutane.

Rule 2. The hydrogen atoms are always substituted at rates which are in the order tertiary > secondary > primary. At 300° C. with reaction in vapour phase these relative rates are 4·43 : 3·25 : 1·00 [29*a*, 1936].

The only serious contradiction to this statement other than the very fragmentary research of Schorlemmer [47, 1868–70] mentioned above is the one made by Ayres [2, 1929] and repeated by Clark [14 1930], to the effect that in the Sharples thermal chlorination of *n*- and isopentanes the substitution of all the hydrogen atoms occurs at the same rate, so that the composition of the monochlorides can be approximately calculated from the number of hydrogen atoms in the various positions. Thus in *n*-pentane there are 6 primary hydrogen atoms and 6 secondary hydrogen atoms, and one would therefore expect —assuming a 'non-selective' chlorination—50% primary and 50% secondary isomers. Ayres and also Clark report 48% primary and 52% secondary chlorides, a very good agreement. As pointed out above, however, neither Ayres nor Clark had attempted an analysis of the chlorides of the pentanes until they had first been converted to alcohols. After the isomeric amyl chlorides had all been synthesized in an extremely pure form and their boiling-points redetermined in this laboratory, it became apparent that 1-chloropentane boils at least 8° C. higher than any of its isomers. With modern laboratory rectification equipment it is a relatively simple matter to separate 1-chloropentane from the other amyl chlorides almost quantitatively and to estimate its concentration in the original mixture. Simultaneously a similar analysis was made of the mixture of *n*- and isopentane used as starting material for the chlorination. The pentane and amyl chloride samples were stated to be representative of the daily production. The pentanes analysed 53% *n*-pentane, 47% isopentane. If 48% of this normal isomer were converted to 1-chloropentane, there would have been 25·44% of 1-chloropentane in the mixed amyl chlorides. Actually, the analysis showed about 12%. This difference is many times the maximum possible experimental error and demonstrates that non-selective chlorination is not obtained. The attached table shows the agreement between observed and calculated isomeric ratios.

TABLE I

Vapour-phase Chlorination of Simple Paraffins at 300° C.

	Isomeric monochlorides %							
	1-chloro		*2-chloro*		*3-chloro*		*4-chloro*	
Hydrocarbon	*Found*	*Calc.*	*Found*	*Calc.*	*Found*	*Calc.*	*Found*	*Calc.*
Propane	48	48	52	52	..	..	..	..
2-Methylpropane	67	67	33	33	..	..	..	..
n-Butane	32	31·6	68	68·4	..	..	..	..
2-Methylbutane	33·5	30·7	22	22	28	32	16·5	15·3
n-Pentane	23·8	23·5	48·8	51	27·4	25·5	..	..

Rule 3. At increasing temperatures there is increasingly close approach to relative rates of 1 : 1 : 1 in both liquid and vapour phase.

This ratio for isobutane is 90% primary : 10% tertiary. At −65° C. (chlorinating photochemically) one obtains 55% tertiary, at +65° C. the yield is 38% tertiary, and at 450° C. about 20% tertiary. The effect at lower temperatures, where no olefine formation occurs, is not complicated by selective pyrolysis, but when operating at high temperatures one can easily confuse a selective pyrolysis of secondary and/or tertiary isomers with a non-selective chlorination. When pyrolysis becomes appreciable, (1) the organic chlorine fails to balance the chlorine present as hydrochloric acid, (2) olefines appear in the recovered hydrocarbon, and (3) especially if recycling is used, chloro-olefines appear in the organic chloride fractions. In an experiment on isobutane using a small steel tube at 450° C. without recycling, a yield of isobutyl chloride was obtained amounting to 99% of the monochloride fraction. This might be taken to indicate that iron is a catalyst favouring primary substitution, were it not that excess hydrochloric acid and olefine formation indicated that the usual percentage of tertiary chloride had been formed and subsequently decomposed. Similar results have been obtained with propane, *n*-butane, and the pentanes. At very high temperatures even in glass apparatus yields of primary chlorides can be obtained equal to or exceeding those calculated on the basis of non-selective chlorination—but always accompanied with excess hydrochloric acid and olefine formation sufficient to account for the result.

Rule 4. Liquid-phase chlorination gives relative rates of tertiary, secondary, and primary substitution which are obtainable only at much higher temperatures in the vapour phase.

This observation has been confirmed in this laboratory with propane, isobutane, pentane, and other hydrocarbons. The fact that a given temperature change produces a much greater effect upon the isomeric ratios in liquid-phase than in vapour-phase reaction may indicate different reaction mechanisms in the two cases.

Rule 5. The presence or absence of the following factors does not affect appreciably the relative rates of tertiary, secondary, and primary substitution: (*a*) moisture, (*b*) carbon surfaces, (*c*) light.

These results seem to indicate that the reaction mechanism is the same whether the chains are initiated by some catalytic effect at the carbon surfaces, by the dissociation of chlorine molecules by absorption of photons, or by simple thermal dissociation of chlorine molecules, and that water does not play any essential role in the system.

Rule 6. Excessive temperatures and/or reaction times result in appreciable pyrolysis of the chlorides in the order tertiary > secondary > primary.

This has already been commented on in connexion with the discussion of Rule 1.

Rule 7. If a molar excess of hydrocarbon is used and chlorination conditions are maintained constant, the yield of monochlorides versus polychlorides may be obtained from the equation $X = KY$, where X is the weight-ratio of monochlorides over polychlorides, Y is the ratio of moles of hydrocarbon over moles of chlorine in the inlet gases, and K is a constant peculiar to each hydrocarbon.

In applying Rule 7 it is assumed that conditions are chosen such that pyrolysis is substantially avoided and all of the chlorine is caused to react.

Rule 8. Dichlorination proceeds by two mechanisms, (1) loss of hydrogen chloride followed by addition of chlorine to the resulting olefine, and (2) progressive substitution. Slow, thermal chlorination favours (1) while with rapid, single-pass thermal reaction or low-temperature photochemical conditions (1) is substantially eliminated.

Rule 9. In vapour-phase chlorination the presence of a chlorine atom (as compared to a methyl group) on a carbon atom tends to hinder further reaction upon that carbon atom during the second substitution.

Relatively small quantities of dichlorides are obtained which contain two chlorine atoms attached to the same carbon atom. These observations have been checked by Ayres, Dr. E. C. Britton and his collaborators of the Dow Chemical Company, by Muskat and Northrup [42, 1930], and also by the writer and by Mr. A. O. Rogers, and are known to hold for the pentanes, propane, isobutane, and *n*-butane. Halogen atoms are considered to be highly 'negative' and the presence of a negative group usually activates the other atoms or groups attached to the same carbon atom. Other negative groups, such as phenyl or carboxyl, activate hydrogen atoms for chlorination. Thus there is in the case of ethylbenzene a strong tendency to chlorinate in the alpha position, only about 10% substituting in the beta position at room temperature and about 45% at 500° C., whereas a non-selective chlorination would require a yield of 60% beta phenethyl chloride.

Perhaps the situation here is complicated by intramolecular rearrangement subsequent to dichlorination, possibly the chlorine does not behave as a negative group in this case. One is reminded of Conant's remark [14, 1932]: 'The fascinating art of organic chemistry will yield only slowly to the devastating inroads of an exact science.'

Rule 10. Herzfelder's Rule (stated in 1893), 'When into a monohalogen compound a second halogen is introduced it always attaches itself to that carbon atom which is situated next to the carbon atom already united with halogen', does not apply to chlorinations and must be replaced in this field by Rules 1 and 9.

Commercial Applications of the Chlorination of Methane and its Homologues

So far as is known to the writer, no one is at present chlorinating methane commercially. Roessler and Hasslacher had a plant at South Charleston, W. Va., just after the war for the chlorination of methane by the Lacy process. The methyl chloride was hydrolysed to methanol. It is understood that the operation was terminated because of the drop in the price of methanol.

The recent demand for ethyl chloride in the preparation of lead tetraethyl has been met by synthesis from the alcohol rather than from ethane [46].

The supposed commercial chlorination of propane in liquid phase dissolved in carbon tetrachloride or propylene dichloride mentioned by Ellis [16] is in fact a chlorination of propylene rather than of propane.

The recent discovery of the anaesthetic value of cyclopropane has resulted in the synthesis of that hydrocarbon in this laboratory from 1,3-dichloropropane which is obtained by the dichlorination of propane. The dichloride is treated with sodium, magnesium, or zinc. The new synthesis has recently operated successfully on a plant scale and has resulted in what is believed to be the first commercial chlorination of propane [29*b*, 1936].

While *n*-butane has not been chlorinated commercially, so far as is known to the writer, some interest is being exhibited in this reaction. On the other hand, the industrial chlorination of isobutane was accomplished in 1932–3 by the Dow Chemical Company at Midland, Michigan. The isobutyl chloride from the chlorination was separated from the tertiary isomer and rearranged to tertiary butyl chloride. The combined tertiary butyl chlorides are used to synthesize tertiary butylphenol, used in the production of tertiary butylphenol-formaldehyde resins [52]. These resins mix with drying oils to form water-resistant varnishes said to possess very superior properties. As a by-product of this chlorination, 1,2-dichloroisobutane containing some of the 1,1 isomer has been placed upon the market to a limited extent. Rather exhaustive tests initiated at Purdue have indicated that another product of this chlorination, 1,3-dichloroisobutane, possesses extraordinary value as a dry-cleaning agent.

Undoubtedly the most important technical development in this field has been the remarkable series of syntheses growing out of the chlorination of the pentanes. This chlorination was pioneered by Brooks, Essex, and Smith [9, 1916], and by Koch and Stallkamp [33, 1927; 34, 1932], but has reached full-scale development at the plant of the Sharples Solvents Corporation now located at Wyandotte, Michigan. The pentanes are first chlorinated thermally and the monochlorides, after rectification, are treated with a mixture of sodium oleate and aqueous caustic soda at 170° C. The sodium oleate aids the conversion both by emulsifying the two immiscible layers, thus assisting the direct hydrolysis by water of the secondary and tertiary chlorides, and by undergoing metathesis with the primary and secondary amyl chlorides, forming the easily saponified amyl oleates. The amyl alcohols are converted to acetates by the usual methods and sold as a high-boiling solvent for nitrocellulose lacquers. The olefines formed as by-products of the hydrolysis are hydrated by means of sulphuric acid to form secondary and tertiary alcohols. Trimethylethylene is also converted to tertiary amylphenol. Less important but interesting products [12, 1933] are diamyl ether, amyl sulphides, amyl mercaptans, used as an odorant in domestic gases, amyl lactate, a high-boiling lacquer solvent, and diamyl phthalate, a lacquer plasticizer.

The methane homologues higher than the pentanes are difficult to obtain in pure form, and their chlorination has been relatively little studied with the exception of a considerable amount of work on paraffin wax. The thermal mono-chlorination of molten paraffin followed by Friedel-Crafts condensation of the monochlorides with naphthalene yields 'Paraflow' [19, 1931]. This material, added in quantities of the order of 1% to a high pour-test lubricating stock, may lower the pour-point by as much as 35° F.

The use of chlorinated waxes as components of flame-proof insulating materials has been patented by Ellis [22, 1917–18], while the production of drying oils by chlorinating higher petroleum fractions with subsequent removal of hydrogen chloride with formation of double bonds has been described by Gardner and Bielouss [25, 1921–2]. The use of chlorinated paraffin wax as a solvent for dichloramine-T has been mentioned by Dakin and Dunham [17, 1918].

TABLE II

Data on Chloro Compounds

Compound	*Boiling-point*	*Melting-point*	*Density*	*Index of refraction*
Chloromethane [7]	−24·09	−91·5	0·91969 at 17·9° C.	..
Dichloromethane [7]	40·1 [21*a*] 41·6	−96·7	1·3222 at 20° C.	1·4237 at $^{20}_{D}$
Trichloromethane [51]	61·2	−63·5	1·49845 at 15° C.	1·44858 at $^{15}_{D}$
Tetrachloromethane [31]	76·75	−22·95	1·60370 at 15° C.	1·46305 at $^{15}_{D}$
Chloroethane [7]	12·2 [21*a*] 13·1	−138·7	0·91708 6/6	..
1,1-Dichloroethane [51]	57·3	−96·6	1·1835 at 15° C.	1·41975 at $^{15}_{D}$
1,2-Dichloroethane [51]	83·50	−35·5	1·26000 at 15° C.	1·44759 at $^{15}_{D}$
1,1,1-Trichloroethane [7]	74·1	..	1·32491 26/4	1·419861 at $^{21}_{D}$
1,1,2-Trichloroethane [7]	113·722	−36·7	1·443 at 20° C.	1·4711 at $^{22}_{D}$
1,1,1,2-Tetrachloroethane [7]	130·49	..	1·588 at 20° C.	1·479 at $^{20}_{D}$
1,1,2,2-Tetrachloroethane [50]	146·2	−43·8	1·60255 at 15° C.	1·49678 at $^{15}_{D}$
Pentachloroethane [50]	162·0	−29·0	1·68813 at 15° C.	1·50542 at $^{15}_{D}$
Hexachloroethane [54]	185	185	2·091 at $^{20}_{4}$	..
1-Chloropropane [6]	46·6 at 770 mm.	−122·8	0·89694 at 15° C.	1·39142 at $^{15}_{\text{He yellow}}$
2-Chloropropane [51]	34·8	−117·0	0·86797 at 15° C.	1·38110 at $^{15}_{D}$
1,1-Dichloropropane [28]	89·6	..	1·143 at 10° C.	1·4320 at $^{20}_{D}$
1,2-Dichloropropane [7] [21]	96·8	..	1·1656 at 14° C.	1·4388
1,3-Dichloropropane [28] [48]	120·4	−99·5	1·201 at 15° C.	1·4499
2,2-Dichloropropane [51]	70·5	−34·4	1·07767 at 15° C.	1·41793 at $^{15}_{\text{He yellow}}$
1,1,1-Trichloropropane [7]	145–150	..	1·417 at 15° C.	..
1,1,2-Trichloropropane [7]	140 [21*a*] 137	..	1·372 at 25° C.	..
1,1,3-Trichloropropane [7]	148	..	1·362 at 15° C.	..
1,2,2-Trichloropropane [7] [28]	123·0	..	1·318 at 25° C.	1·4630
1,2,3-Trichloropropane [7]	156	−14·7	1·417 at 15° C.	..
1,1,1,2-Tetrachloropropane [7]	152–153	−65	1·473 at 20° C.	1·4867
1,1,1,3-Tetrachloropropane [7]	..	..	..	..
1,1,2,2-Tetrachloropropane [7]	153	..	1·47 at 13° C.	..
1,1,2,3-Tetrachloropropane [7]	179–180 at 756 mm.	..	1·521 at 15° C.	..
1,2,2,3-Tetrachloropropane [7]	164	..	1·496 at 17° C.	..
1,1,1,2,3-Pentachloropropane [7]	179–180	..	..	..
1,1,2,3,3-Pentachloropropane [7]	198–200	..	1·6086 at $^{34}_{4}$	1·5131 at $^{16·5}_{D}$
1,1,1,2,3,3-Hexachloropropane [7]	216	..	1·6980 at $^{34}_{4}$	1·5250 at $^{17}_{D}$
1,1,2,2,3,3-Hexachloropropane [7]	218·5	..	1·7137 at $^{34}_{4}$	1·5262 at $^{17}_{D}$
1,1,1,2,2,3,3-Heptachloropropane [7]	164 at 90 mm.	29·4	1·8048 at $^{34}_{4}$	..
1,1,1,2,3,3,3-Heptachloropropane [7]	249	11–11·5	1·7921 at $^{34}_{4}$	1·5427 at $^{21}_{D}$
Octochloropropane [7]	268–269 at 734 mm.	160	..	..
1-Chlorobutane [51]	78·5	−123·1	0·89197 at $^{15}_{4}$	1·40499 at $^{15}_{\text{He yellow}}$
2-Chlorobutane [51]	68·25	−131·3	0·87880 at 15° C.	1·39940 at $^{15}_{D}$
1-Chloro-2-methylpropane [51]	68·85	−131·2	0·88290	1·40096 at $^{15}_{D}$
2-Chloro-2-methylpropane [51]	50·7 at 760 mm.	−27·1° atm. press.	0·82935 at $^{30}_{4}$	1·38689 at $^{17·8}_{D}$
1,1-Dichlorobutane [7]	113–115	..	..	..
1,2-Dichlorobutane [20]	121–122 at 725 mm.	..	..	..
1,3-Dichlorobutane [7]	134	..	..	..
1,4-Dichlorobutane [29]	155·0 at 760 mm.	..	..	..
2,2-Dichlorobutane [7]	95–97	−74	..	1·4295 at $^{20}_{D}$
2,3-Dichlorobutane (d1) [26]	119·5	..	1·1051 at 25° C.	1·4458 at $^{15}_{\beta}$
1,1-Dichloro-2-methylpropane [39]	103–105	..	1·0111 at 12° C.	..
1,2-Dichloro-2-methylpropane [39]	107	..	1·094 at 20° C.	..
1,3-Dichloro-2-methylpropane [39]	136·0	−62–3	1·13 at 20° C.	..
1,2,3-Trichlorobutane [7]	79–80 at 32 mm.	..	1·3241	..

TABLE II (*cont.*)

Compound	*Boiling-point*	*Melting-point*	*Density*	*Index of refraction*
1,2,2,3-Tetrachlorobutane [7]	85 at 10 mm.	..	..	..
1,2,3,3-Tetrachlorobutane [11]	55–57 at 10 mm.	..	1·4204	1·4958
1,2,3,4-Tetrachlorobutane [7]	130–140 at 50 mm.	72·5–73	..	..
1,2,3,3,4-Pentachlorobutane [11]	85 at 10 mm.	..	1·5543	1·5157
1-Chloropentane [37]	108·35	−99	0·88657 at $^{15}_{4}$	1·41192 at $^{20}_{D}$
2-Chloropentane [7] [55]	96·6–96·8	..	0·891 at 21° C.	1·4062 at $^{19·5}_{D}$
3-Chloropentane [26]	97·2 [55]	..	0·8967 at 14·5° C.	1·4163 at $^{14·5}_{D}$
1-Chloro-2-methylbutane [1]	99·9 [55]	..	0·8812	..
2-Chloro-2-methylbutane [1]	85·5–85·8	−72·9	0·8692 at 15° C.	1·407 at $^{18}_{D}$
1-Chloro-3-methylbutane [1]	98·8 [55]	..	0·8928 at 0° C.	1·41118 at $^{18}_{D}$
2-Chloro-3-methylbutane [31]	93·0	..	0·8752 at $^{15}_{15}$	1·4095 at $^{20}_{D}$
1-Chloro-2,2-dimethylpropane [58]	84·4	−20∓1° C.	0·866 at $^{20}_{4}$	1·4042 at $^{20}_{D}$
1,4-Dichloropentane [7]	59–61 at 17 mm.	..	..	..
1,5-Dichloropentane [48]	182·3 at 760 mm.	−72·8	1·10158 at $^{15}_{4}$	1·46161 He yellow
2,2-Dichloropentane [5]	128–129	..	1·04 at 20° C.	1·434 at $^{20}_{D}$
2,3-Dichloropentane [7]	138–139	..	..	..
2,4-Dichloropentane [6]	147–150	..	1·063 at 18° C.	1·477 at $^{18}_{D}$
1,4-Dichloro-2-methylbutane [7]	170–172	..	..	..
2,3-Dichloro-2-methylbutane [7]	130–135	..	1·068 at $^{15}_{4}$	1·445 at $^{18}_{D}$
2,4-Dichloro-2-methylbutane [7]	152–154	..	1·0654 at $^{20}_{4}$	..
3,3-Dichloro-2-methylbutane [31]	145	..	1·065 at $^{20}_{4}$	..
3,4-Dichloro-2-methylbutane [7]	143–145	..	1·0923 at $^{17·5}_{0}$	..
4,4-Dichloro-2-methylbutane [7]	130	..	1·05 at 24° C.	..
2,3,3-Trichloro-2-methylbutane [5]	176	..	1·215 at $^{15}_{4}$	1·472 at $^{21}_{D}$
Tetrachloro-2-methylbutane [7]	220–225	..	1·427 at 10° C.	..
1,3,2,'2'′-Tetrachloro-2,2-dimethylpropane [7]	110 at 12 mm.	97° C.	..	..
3,3,4,4,4-Pentachloro-2-methylbutane [7]	235–240	..	..	..
1-Chlorohexane [7]	134–135 at 760 mm.	..	0·87551 at $^{20}_{4}$	1·41944 at $^{20}_{D}$
2-Chlorohexane [7]	122·5 at 754 mm.	..	0·8694 at $^{21}_{4}$	1·4142 at $^{21·5}_{D}$
2-Chloro-2-methylpentane [7]	110–113	..	0·8678 at $^{15}_{4}$	1·41476 at $^{16}_{D}$
3-Chloro-3-methylpentane [7]	116° C.	..	0·8893 at $^{14}_{4}$	1·42315 at $^{16·5}_{D}$
5-Chloro-2-methylpentane [7]	125–126 at 761 mm.	..	..	..
1-Chloro-2,3-dimethylbutane [7]	122	..	0·8943 at 14° C.	..
2-Chloro-2,3-dimethylbutane [7]	112·1	−10·4	0·8749 at 20° C.	..
3-Chloro-2,2-dimethylbutane [6]	113–114	..	..	..
1,2-Dichlorohexane [7]	172–174	..	1·085 at 15° C.	..
1,5-Dichlorohexane [7]	74–8 at 10 mm.	..	..	..
1,6-Dichlorohexane [7]	203–205	..	..	..
2,3-Dichlorohexane [7]	162–165	..	1·0527	..
2,5-Dichlorohexane [7]	170–180	..	..	..
3,3-Dichloro-2,2-dimethylbutane [7]	..	151	..	..
1,2,3,4,5,6-Hexachlorohexane [7]	180–185 at 30 mm.	137·5	..	..

REFERENCES

1. ASCHAN, O. *Chem. Abs.* **14,** 3654 (1920).
2. AYRES, E. E. *Ind. Eng. Chem.* **21,** 899 (1929).
3. —— U.S.P. 1,717,136; 1,741,393.
4. —— U.S.P. 1,835,202 (8 Dec. 1931).
5. BAURGUEL. *Compt. rend.* **177,** 823 (1923).
6. *Beilstein,* vol. **1,** Syst. 5, i. 34–60 (supplement).
7. *Beilstein,* vol. **1,** Syst. 5, pp. 60–152.
8. BOSWELL, M. C., and MCLAUGHLIN, R. R. *Canad. J. Research,* **1,** 240 (1929).
9. BROOKS, B. J., ESSEX, H., and SMITH. U.S.P. 1,191,916 (18 July 1916), *Chem. Abs.* **10,** 2297.
10. BUTLEROV, A. *Ann.* **144,** 15–17 (1867).
11. CAROTHERS, W. H., and BERCHET, G. J. *J.A.C.S.* **55,** 622 (1933).
12. Chemicals Derived from the Pentanes. *Ind. Eng. Chem.,* News Edition, **11,** no. 22, p. 334 (20 Nov. 1933).
13. CLARK. *Ind. Eng. Chem.* **22,** 439 (1930).
14. CONANT, J. B. *Ind. Eng. Chem.* **24,** 472 (1932).
15. CURME, G. O. U.S.P. 1,315,547, *Chem. Abs.*
16. —— U.S.P. 1,422,838. *J.S.C.I.* **41,** 686 A (1922).
17. DAKIN, H. D., and DUNHAM, E. K. *Brit. Med. J.* **1,** 51 (1918).
18. DAVIS, H. S. U.S.P. 1,815,022 (1931); *Ind. Eng. Chem.* **23,** 1452 (1931); *Nat. Petr. News,* **24** (52), 32, 34 (1932).
19. DEANESLY, R. M. *J.A.C.S.* **56,** 2501 (1934). See also B.P. 399,991.
20. DE MONTMOLLIN, M., and MATILE, P. *Helv. chim. Acta,* **7,** 106 (1924).
21. ELLIS, C. *The Chemistry of Petroleum Derivatives,* 718. Chemical Catalog Company, New York.

21*a*. —— Ibid. 467.

22. ELLIS, C. U.S.P. 1,246,810 (1917), *Chem. Abs.* **12,** 298 (1918).
23. FAVORSKII, A. E., and ZALESSKII-KIBORDINE, J. *Bull. Soc. chim.* **37,** 1227 (1925).
24. FLEMING, G. N., and WHITMORE, F. C. *J.A.C.S.* **54,** 3460 (1932).
25. GARDNER, H. A., and BIELOUSS, E. *Ind. Eng. Chem.* **14,** 619 (1922); U.S.P. 1,384,447 (1921) and 1,412,399 (1922).
26. GRIGNARD, V., and KASHICHI ONO. *Bull. Soc. chim.* **39,** 1589 (1926).
27. HASS, H. B., and WEBER, P. *Ber.* **67,** 974 (1934).

27*a*. HASS, H. B., MCBEE, E. T., and WEBER, P. *Ind. Eng. Chem.* **27,** 1190 (1935).

28. HASS, H. B., and CHAO. Unpublished work.
29. HASS, H. B., and TONER. Unpublished work.

29*a*. HASS, H. B., MCBEE, E. T., and WEBER, P. *Ind. Eng. Chem.* **28,** 333 (1936).

29*b*. HASS, H. B., MCBEE, E. T., HINDS, G. E., and GLUESENKAMP, E. W. *Ind. Eng. Chem.* **28,** 1178 (1936).

30. HERZFELDER, A. D. *Ber.* **26,** 2432 (1893).
31. *International Critical Tables,* **1,** 192.
32. JONES, G. W., ALLISON, V. C., and MEIGHAN, M. H. U.S. Bureau of Mines Tech. Paper, 225 (1921).
33. KOCH, G. T., and BURRELL, G. A. *Ind. Eng. Chem.* **19,** 442 (1927).
34. KOCH, G. T., and STALLKAMP, A. L. U.S.P. 1,380,067, *Chem. Abs.* **15,** 3393. KOCH, G. T. U.S.P. 1,432,761 (24 Oct. 1932), *Chem. Abs.* **17,** 289.
35. LACY. U.S.P. 1,111,842; 1,190,659; 1,242,208; 1,253,055; 1,263,906; 1,286,353; 1,308,760; 1,816,845; 1,834,089; 1,914,135; 1,915,354; 1,939,292 Re 14,105.

36. Lunt, G.P. U.S.P. 1,824,558 (22 Sept. 1931), *Chem. Abs.* **26,** 150 (1932).
37. Luther, R., and Goldberg, E. *Z. physik. Chem.* **56,** 43 (1906).
38. Mabery, C. F., and Hudson, E. J *Amer. Chem. J.* **19,** 243–62 (1897).
39. McBee, E. T. Ph.D. Thesis, Purdue University. *Ind. Eng. Chem.* **27,** 1190–5 (1935); **28,** 333–9 (1936).
40. Mason, J., and Wheeler, T. S. *J.C.S.* 2282 (1931).
41. ——— *J.C.S.* 2282 (1931).
42. Muskat, T. E., and Northrup, H. E. *J.A.C.S.* **52,** 4043 (1930).
42*a*. Navez, L. *Bull. Soc. Chim. Belg.* **39,** 435–43 (1930).
43. Pease, R. N., and Walz, G. F. *J.A.C.S.* **53,** 3728 (1931).
44. Pfeifer, J., Mauthner, F., and Reitlinger, O. *J. pr. Chem.* **99,** 239 (1919); *J.S.C.I.* **38,** 924 A (1919).
45. Private communication from Mr. Ayres and Mr. Clark, and Mr. C. A. Thomas, Director of Research for Sharples Solvents.
46. Private information from Dr. Midgley.
47. Schorlemmer, C. *Proc. Roy. Soc.* **16,** 35 (1868); *Ann.* **150,** 210 (1869); *Ann. chim. phys.* **19,** 439 (1870).
48. Serwy, H. *Bull. Soc. chim. Belg.* **42,** 483 (1933).
49. Simon. *Bull. Soc. chim. Belg.* **38,** 47 (1929).
50. Sutherland, B. P., and Maass, O. *Trans. Roy. Soc. Can.* **20,** 499 (1926).
51. Timmermans, J., and Martin, F. *J. chim. phys.* **23,** 747 (1926); **25,** 411–51 (1928); **31,** 85–124 (1934); **27,** 401 (1930).
52. U.S.P. 1,800,295; 1,800,296; B.P. 334,572; F.P. 592,548; G.P. 440,003 and 548,656.
53. U.S.P. 1,954,438.
54. Van Nostrand. *Chem. Annual,* 362 (1922).
55. Weber, Paul. Ph.D. Thesis, Purdue University, *The Chlorination of* n-*Pentane and* iso-*Pentane. Ind. Eng. Chem., Anal. Ed.* **7,** 231 (1935); *Ind. Ed.* **27,** 1190–5 (1935); **28,** 333–9 (1936).
56. Wertyporoch. *Ber.* **66,** 732 (1933).
57. Weston, P. E., and Hass, H. B. *J.A.C.S.* **54,** 3337 (1932).
58. Whitmore, F. C., and Fleming, G. H. *J.A.C.S.* **55,** 4161 (1933).
59. Whitmorf, F. C., and Johnson, F. *J.A.C.S.* **55,** 5020 (1933).
60. Yuster, S., and Reyerson, L. H. *J. Phys. Chem.* 1935.

CHEMICALS DERIVED FROM PENTANES

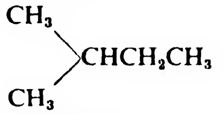
By **CHAS. ALLEN THOMAS, A.B., D.Sc.**

Director of Research, Thomas and Hochwalt Laboratories, Research Division, Monsanto Chemical Company.

PRACTICALLY all natural gas gasolines contain varying amounts of pentanes. Examinations of samples from many localities, including Texas, Oklahoma, Kansas, Kentucky, Ohio, and West Virginia, have revealed the presence of pentanes in substantial proportions. There exist three pentanes, namely,

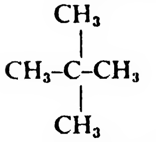
$CH_3CH_2CH_2CH_2CH_3$ b.p. 36·15° C.

n-Pentane



b.p. 27·95° C.

Isopentane



$CH_3\text{–}C(CH_3)_2\text{–}CH_3$

b.p. 9·5° C.

Neopentane

The natural gasolines usually contain from 20 to 40% of *n*- and isopentanes, which usually occur in equal proportions, but not more than doubtful traces of neopentane. Therefore, below the boiling-point of isopentane (27·95° C.) the only saturated hydrocarbon found is *n*-butane boiling at 0·6° C. Above the boiling-point of *n*-pentane (36·15° C.) the next saturated chain hydrocarbon is trimethyl-ethyl-methane, boiling at 49·7° C. Natural gas gasolines generally contain no unsaturated chain hydrocarbons or cyclic compounds boiling below the hexanes.

It is therefore evident that the recovery of a comparatively pure mixture of *n*- and isopentane by fractional distillation is relatively simple, and this mixture can be obtained in abundance as a raw material for commercial syntheses. Paraffin hydrocarbons of this type are too stable to enter directly into chemical syntheses. To make them sufficiently reactive, there are, at the present time, three main avenues of approach:

(1) Pyrolysis: splitting out some of the hydrogen to form olefines;
(2) Oxidation: formation of aldehydes, ketones, acids, and alcohols; and
(3) Chlorination: employing the resulting chlorides as intermediates.

This article will deal only with chlorination of pentane and some subsequent derivatives of the resulting amyl chlorides.

Chlorination of aliphatic hydrocarbons fills a voluminous part of chemical literature which has been amply reviewed by Egloff, Schaad, and Lowry [4, 1931], and Carleton Ellis in his book, *The Chemistry of Petroleum Derivatives* [5, 1934]. The general methods used for chlorination of hydrocarbons are as follows:

(1) Photochemical.
(2) Thermal.
(3) Catalytic.
(4) Reaction with chemical compounds which liberate chlorine.
(5) Silent electric discharges, and
(6) Various combinations of the above.

In the Sharples plant at Wyandotte, Michigan, a mixture of *n*- and isopentane is chlorinated in the vapour phase in total darkness and without a catalyst. The present plant is capable of feeding 22 tons of chlorine per day continuously into a 60-mile per hour stream of hot pentane vapour. One hundred thousand gallons of pentanes pass through the reaction zone every day, but at any given moment only 3 gallons of pentanes and not more than 8 oz. of free chlorine are in contact in the reaction zone.

In operating a plant involving chlorination, it must ever be borne in mind that for every molecule of aliphatic chloride produced, a molecule of hydrogen chloride must be successfully removed from the system without undue corrosion of the plant equipment. Ayres [1, 1929], Clark [3, 1930], and Bohall [2, 1932] have amply described this engineering accomplishment. Fractionated pentane is supplied in tank cars to the plant by natural gasoline refiners. This cut boils between 28 and 39° C. and is approximately an equal mixture of *n*- and isopentane. As shown in the flow sheet (Fig. 1), this pentane is pumped from storage to a mixing tank, to which the pentanes recovered from the system are also added, and the mixture is thoroughly dehydrated. The pentanes are then passed through one vaporizer while chlorine is passed through another, and the two gas streams are combined in a mixing throat from which they are led into an externally heated pipe-still. The exit gases from the pipe-still pass through another bank of pipes which are cooled with spray water and then enter the first of four continuous fractionating columns. This first column takes overhead only pentanes and hydrochloric acid produced in chlorination. The product is returned to the mixing tank at the start of the system, while from the bottom of the column a mixture of amyl chlorides and unchlorinated pentane continues to a second continuous fractionating column. Here the process is repeated, the pentane rich overhead distillate returning to the feed of the first column, while the highly chlorinated products pass to the third column. Here it is that the amylene dichlorides and polychlorides are removed in the still liquor and sent to a separate still, while the amyl chlorides are sent to the fourth column. From this last column a practically pure mixture of amyl chloride is obtained from the bottom of the column, while a small amount of residual pentane is taken overhead with some amyl chloride, which is subsequently returned to the first still.

The hydrochloric acid and unchlorinated products taken overhead from the first still return to the bottom of the mixing tank, and this dry hydrochloric acid bubbling up through the pentanes thoroughly dehydrates the pentane. The hydrochloric acid formed settles to the bottom of the tank where it can be drawn off. Only a very small portion of the hydrochloric acid produced is removed in this way, the rest being recovered in a continuous system which takes the gas from the top of the mixing tank, passes it through a condenser to remove most of the pentane, and then through a countercurrent absorption system of fused silica in which the hydrochloric acid is absorbed in water. The exit gas from this absorbing system is thoroughly scrubbed with dilute caustic brine liquor which results from hydro-

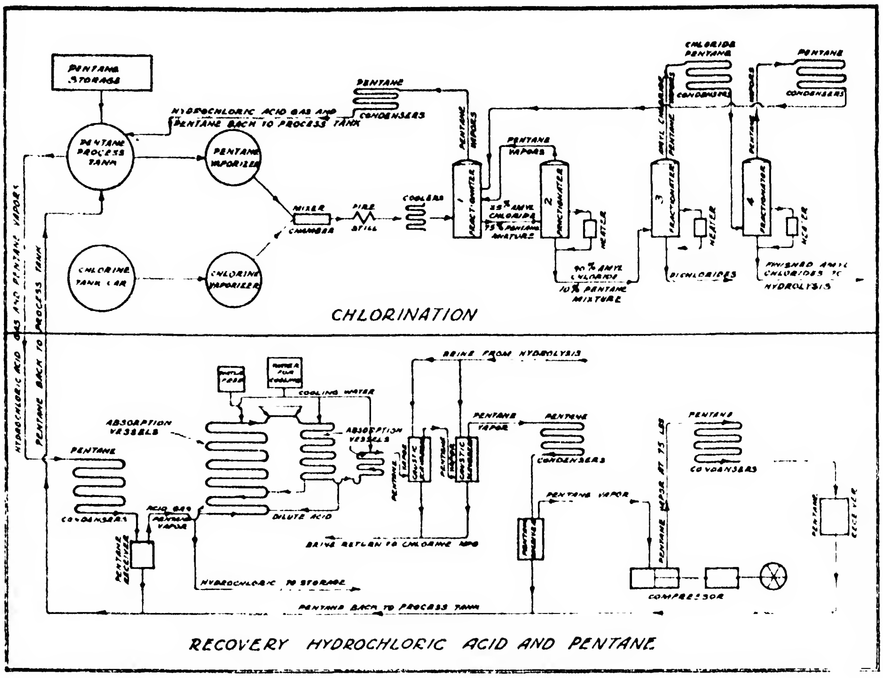


FIG. 1.

lysis operations described later. The Sharples plant adjoins the chlorine-producing plant of the Pennsylvania Salt Company, and the neutral brine is piped back to them for subsequent chlorine manufacture. The scrubbed gases pass through a condenser, are compressed, and the liquid pentanes are returned to the mixing tank. The hydrochloric acid obtained is 20° Bé. and is run from the absorption system into storage and sold.

There are several products synthesized from the resulting mixture of amyl chlorides. The product most important in tonnage is amyl alcohol, which is subsequently acetylated to yield amyl acetate. For the production of amyl alcohol the mixture of amyl chlorides is hydrolysed with a caustic solution in the presence of a catalyst. Fig. 2 is a flow sheet showing how this process is carried out in a continuous system. A 30% caustic solution is fed into the digester of the mixed amyl chlorides and the products of the reaction are removed from the second digester which is operated only partially full. Amyl alcohol, amyl chloride, and amylene are taken off in vapour form from these digesters, condensed, and thoroughly fractionated in a series of continuous columns. Amylenes are one of the by-products of this reaction which go into other processes which are discussed later. A large part of the amyl alcohols produced is acetylated to form amyl acetate.

One of the most troublesome engineering problems was that of corrosion. Originally the equipment was of copper, but later was replaced by iron. It has been found that iron stands up well as long as the gases are perfectly dry, but with a small amount of moisture corrosion from hydrochloric acid is very rapid. Strict care is maintained to keep the chlorine entering the plant perfectly dry and the pentane thoroughly dehydrated with dry hydrochloric acid before entering the mixing tank.

It is rather difficult to analyse the resulting chlorides, because, when subjected to distillation, they readily rearrange and decompose. This probably accounts for the divergent reports in the literature of the products obtained. Fig. 3 shows the configuration of *n*- and isopentanes and their monochlorides. It is our opinion that by chlorinating pentanes in the dark, at high temperature, in the vapour phase, and continuously, the chlorides tend to form according to the mathematical laws of probability. They may rearrange after being formed, but the initial substitution of hydrogen by chlorine seems to be governed by the laws of probability. This is in general agreement with the conclusions of Hass [6; 7, 1934; 8, 1932]. Therefore, if we consider the possibilities in the case of *n*-pentane, there are theoretically 6 chances in 12 of forming 1-chloropentane. In the case of 2-chloropentane, there are 4 chances out of 12, or 33⅓% theoretical probability of forming this chloride. In the case of isopentane, there are 3 out of 12 chances of forming 4-chloro-2-methylbutane and a 25% yield should be obtained. By the same reasoning, there is a 50% chance of forming 1-chloro-2-methylbutane. Similarly, there is $\frac{2}{12}$ or 16⅔% chance of forming 3-chloro-2-methyl-

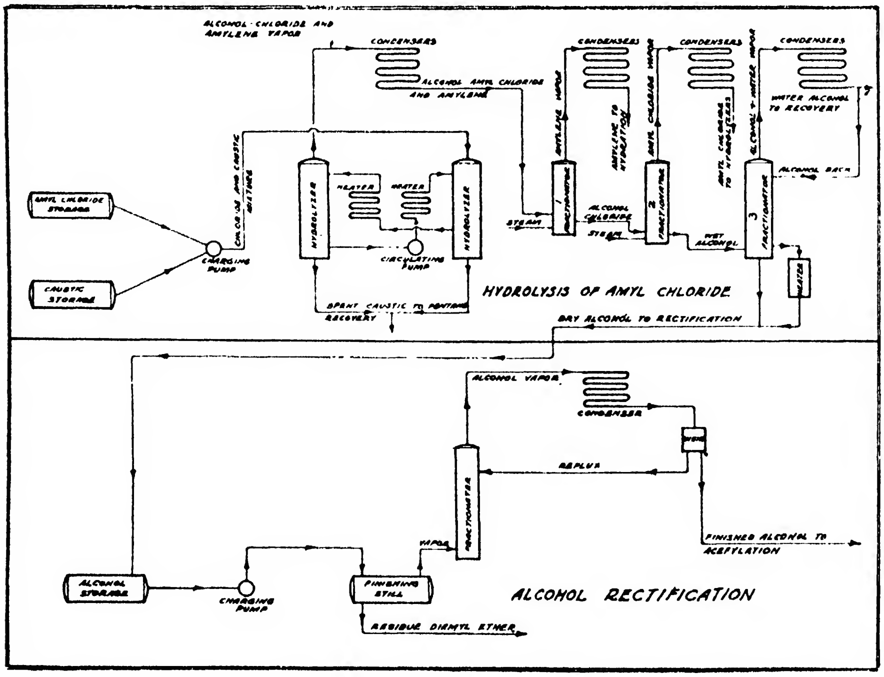
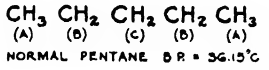


FIG. 2.

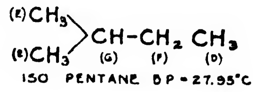
butane and $\frac{1}{12}$ or 8⅓% chance of forming 2-chloro-2-methylbutane. In actual plant practice the two isomers of pentane are chlorinated together—an equal molecular mixture of *n*- and isopentane being employed. No attempt is made to separate the individual chlorides, and the whole is subjected to hydrolysis with sodium hydroxide and an oleate emulsifying agent. Due to the formation of amylenes which are removed from the system, in both the chlorination and hydrolysis steps, it is impossible to give the exact yields of the various chlorides.

It is also very difficult to fractionate the chlorides even under vacuum with any degree of accuracy, because of the unstability of the secondary and tertiary chlorides and the rearrangement taking place. However, several careful fractionations of the resulting alcohols from the plant have been performed. If we assume that the alcohols were derived from the corresponding chlorides, the actual results will compare with the theoretical as shown in Fig. 3. There is a good deal of doubt as to the existence of methyl isopropyl carbinol; some workers report that there is none of this alcohol present, whereas others report 5·2%. This chloride may be formed, but possibly it rearranges immediately to the tertiary chloride, or to amylene. It will be noticed that the total amount of primary alcohols in this mixture is approximately 57%. As the gap between the boiling-point of the high secondary alcohol (119·6° C.) and the lowest primary alcohol (127·5° C.) is large, there is every reason to believe that the 57% value is reasonably correct. It is impossible to know exactly the degree with which the various isomeric chlorides break down into amylene. We cannot assume that all the primary chlorides, being more stable, are completely converted into alcohols and that the entire amylene formation is a result of breaking down of the secondary and tertiary compounds. The best deductions on this work assume that 80% of the original primary chlorides are converted to the corresponding alcohols, whereas only 50% of the secondary and tertiary chlorides are converted.



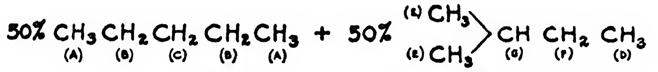
NORMAL PENTANE B.P. = 36.15°C

	THEORETICAL
(A) 1-CHLOROPENTANE B.P = 107°C	$\frac{6}{12}$ = 50%
(B) 2-CHLOROPENTANE B.P = 97°C.	$\frac{4}{12}$ = 33⅓%
(C) 3-CHLOROPENTANE B.P = 96°C	$\frac{2}{12}$ = 16⅔%



ISO PENTANE B.P = 27.95°C

	THEORETICAL
(D) 4-CHLORO-2-METHYL BUTANE B.P = 101°C	$\frac{3}{12}$ = 25%
(E) 1-CHLORO-2-METHYL BUTANE B.P = 99°C.	$\frac{6}{12}$ = 50%
(F) 3-CHLORO-2-METHYL BUTANE B.P = 91°C.	$\frac{2}{12}$ = 16⅔%
(G) 2-CHLORO-2-METHYL BUTANE B.P = 86°C	$\frac{1}{12}$ = 8⅓%



		THEORETICAL	ACTUAL
(A) 1-CHLORO-PENTANE		25%	24.3%
(B) 2-CHLORO-PENTANE		16⅔%	15.2%
(C) 3-CHLORO-PENTANE		8⅓%	18.6%
(D) 4-CHLORO-2-METHYL	BUTANE	12½%	18.6%
(E) 1-CHLORO-2-METHYL	BUTANE	25%	14.3%
(F) 3-CHLORO-2-METHYL	BUTANE	8⅓%	5.2%
(G) 2-CHLORO-2-METHYL	BUTANE	4⅙%	3.8%

FIG. 3.

Since the primary alcohols are the best lacquer solvents, they are, at the present writing, more interesting commercially. The various alcohols from *n*- and isopentane are given below with their boiling-points.

From n-Pentane

$CH_3CH_2CH_2CH_2CH_2OH$

Normal butyl carbinol	b.p. 137·9° C.
Pentanol-1	sp. gr. 0·817 at 20°/4°

$CH_3\overset{*}{C}HOHCH_2CH_2CH_3$

Methyl propyl carbinol	b.p. 119·5° C.
Pentanol-2	sp. gr. 0·809 at 20°/4°

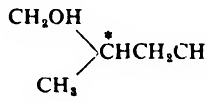
$CH_3CH_2CHOHCH_2CH_3$

Diethyl carbinol	b.p. 115·6° C.
Pentanol-3	sp. gr. 0·815 at 20°/4°

From Isopentane

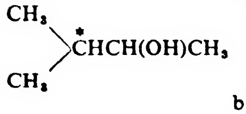
$\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!CHCH_2CH_2OH$

Isobutyl carbinol	b.p. 130·5° C.
Primary isoamyl alcohol	sp. gr. 0·8129 at 15°/4° C.



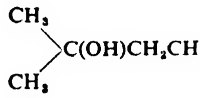
$\begin{matrix}CH_2OH\\CH_3\end{matrix}\!>\!\overset{*}{C}HCH_2CH_3$

Secondary butyl carbinol	b.p. 128° C.
Active amyl alcohol	sp. gr. 0·8169 at 20°/4° C.



$\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!\overset{*}{C}HCH(OH)CH_3$

Methyl isopropyl carbinol	b.p. 112·9–114° 113·9° C.
Secondary isoamyl alcohol	sp. gr. 0·819 at 20°/4° C.



$\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!C(OH)CH_2CH_3$

Dimethyl ethyl carbinol	b.p. 101·8° C.
Tertiary amyl alcohol	sp. gr. 0·809 at 20°/4° C.

Three of the seven alcohols have asymmetric carbons which are indicated by an asterisk (*). However, the synthetic product contains only the racemic form and therefore is not optically active.

The difference in activity of these various amyl alcohols is worthy of comment. In general, the most reactive is the tertiary, then the secondary, and finally the primary alcohols. However, this reactivity depends mainly on the type of reaction to which they are subjected. For example, the primary alcohols react vigorously with sodium to yield the corresponding alcoholates, the secondary less so, and the tertiary scarcely at all. The rate of esterification also parallels the reactivity of the alcohols and can be explained by assuming that the primary alcohols ionize to RO^-H^+ and the tertiary alcohols ionize to R^+OH^-, while the secondaries probably give both types of ionization.

Amyl alcohol is the starting-point in the manufacture of various esters which are used as solvents and plasticizers. By far the most important of these esters is amyl acetate, which is made from a mixture of the various isomeric alcohols and acetic acid, and is known to the solvent trade as Pentacetate. Because of its comparatively high boiling-point it has high blush resistance and good flowing qualities which impart a smooth finish to the lacquer film. Tartaric acid can be esterified with a mixture of amyl alcohols to form diamyl tartrate which boils at 205 to 208° C. at 30 mm. This ester, along with amyl stearate and diamyl phthalate, is of commercial interest as a plasticizer.

When a mixture of these isomeric amyl alcohols, known to the trade as Pentasol, is treated with potassium hydroxide and carbon bisulphide, potassium amylxanthate is formed which is used in the ore-flotation field.

The mixed amyl chlorides are used as the starting-point in the synthesis of other compounds. For instance, when treated with potassium cyanide, amyl cyanide, boiling between 125 and 155° C., is formed. This cyanide yields caproic acid on hydrolysis. These alkyl chlorides enter into several Friedel and Crafts reactions, one of which produces amylnaphthalene and diamylnaphthalene.

One of the most important commercial derivatives of amyl chloride is amyl mercaptan, produced by treating amyl chloride with sodium hydrogen sulphide. This isomeric mercaptan is a liquid of pronounced disagreeable odour having a boiling-point between 100 and 127° C. Its use as an odorant in natural gas is increasing.

As an industry, gas manufacturers have long appreciated the value of odour in coal gas and carbonated water gas. These odours being inherent in the gas, users quickly learn to associate the odour with the gas. Usually people give little consideration to the atmosphere surrounding them if no unusual or irritating odour is present. Attention is quickly attracted, however, to unusual odours, uncomfortable breathing, or eye irritations, for experience has justified caution in such cases.

Natural gas, carburetted propane or butane, as well as mixed manufactured and natural gases, are increasingly replacing odorous types. The protection of the natural and familiar odour is missing. Artificial odour protection is the obvious substitute. Amyl mercaptan is the basis of a new gas odorant known to the trade as Pentalarm. Very small amounts are necessary, 0·7 lb. being sufficient to odorize a million cubic feet of natural gas. The Pentalarm is metered into the gas main by a special equipment which operates by by-passing a controlled proportion of the gas around an orifice plate, saturating this by-passed gas with Pentalarm, and then returning it to the main gas stream.

The reduction in gas losses as the result of leaks found through odorization is worthy of consideration for, in many towns where odorization has continued for a week or ten days, street and line leaks have shown up through the ground itself.

Amyl chlorides under proper conditions react with ammonia to form amines. The boiling-points of the mono-, di-, and triamylamines are sufficiently far apart to permit easy separation by distillation. This is not the case with the lower aliphatic amines, such as methylamine, where the boiling-point of the mono-derivative is higher than that of the di, and the tri is about the same as that of the mono. The amines offer a convenient starting material for a host of interesting syntheses.

The amines are strong organic bases, a molar solution of monoamylamine having a *pH* of 11·67 compared with 11·62 for a molar ammonium hydroxide solution. Monoamylamine is completely miscible with water and is a powerful organic solvent of about the same order of magnitude as pyridine. Diamylamine is only slightly soluble in water, while triamylamine is practically insoluble.

These amines enter into all the typical reactions of amines. They can be condensed with aldehydes, ketones, and oxides. The hydrogen of monoamylamine and diamylamine is readily replaceable with metallic sodium. Monoamylamine reacts with metallic sodium on warming, one hydrogen atom being replaced by sodium, giving sodium amyl amide. The amines also react with phosgene, urea, cyanic acid, thiocyanic acid, and isocyanates to give ureas and thio-ureas. Being strong organic bases, the amyl amines react readily with fatty acids to form organic soaps. These soaps have excellent emulsifying properties, a small quantity being capable of causing the suspension of a large quantity of oil in water.

Diamyl nitrosamine, prepared by reacting nitrous acid with diamylamine, is a high-boiling liquid which has the ability to markedly inhibit the corrosion of metals by hydrogen sulphide.

Other interesting derivatives of the amyl chlorides are those formed by their reaction with benzene, naphthalene, aniline, phenylenediamines, diphenylamine, benzylamines, phenol, cresols, and other related compounds. It is thus possible to prepare a whole series of mixed aliphatic aromatic derivatives which can serve as raw materials for other syntheses.

In hydrolysing the mixed amyl chlorides, some of them decompose to form amylenes. Perhaps all of the five possible amylenes are formed during this hydrolysis, but here again a rearrangement takes place and the two main products obtained are pentene-2 and trimethylethylene. It has been found that pentene-2 is the stable configuration for the 5-carbon straight chain olefin, and that pentene-1 can be rearranged by heat to pentene-2. Likewise, isopropylethylene and unsymmetrical-methylethylethylene apparently rearrange to the stable configuration of the branched chain, trimethylethylene. This is graphically shown in Fig. 4.

The reactivity of these two olefines is interesting. Pentene-2 on hydrolysis with sulphuric acid forms a mixture of diethyl and methyl propyl carbinol, with the latter predominating. The hydrolysis of trimethylethylene with sulphuric acid gives only tertiary amyl alcohol. With hypochlorous acid, pentene-2 reacts, with the chlorine entering the 3 position, while the hydroxyl group goes in the 2 position. With trimethylethylene the hydroxyl group goes on to the tertiary carbon, while the chlorine goes to the secondary carbon. The corresponding oxides made from these chlorohydrins follow the general rule that the more branched the chain the smaller the stability, for the oxide from trimethylethylene is less stable than that from pentene-2.

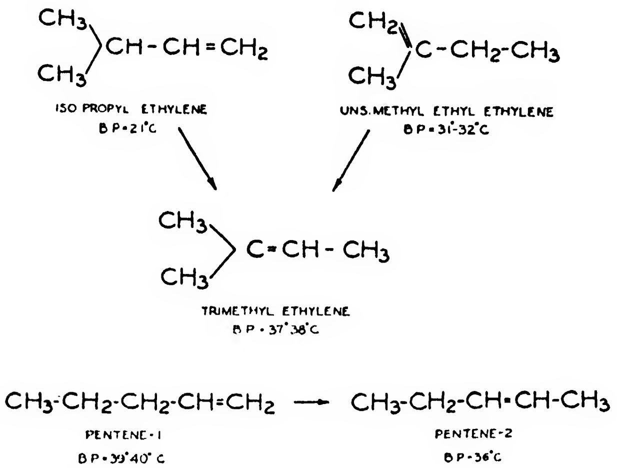


FIG. 4.

The reaction of trimethylethylene with phenol (Fig. 5) in the presence of sulphuric acid to make tertiary-amylphenol is particularly interesting, as this product is finding considerable use in the manufacture of oil-soluble phenol-formaldehyde-type resins. In the case of trimethylethylene it is assumed that the reaction takes place to form an intermediate (tertiary-amyl phenyl ether) which rearranges to form the tertiary-amylphenol. However, this ether has never been isolated. In the case of a secondary olefine, such as pentene-2, the ether formed is fairly stable and only with heat does it rearrange to form the secondary amylphenol. The primary ether has been prepared by reacting *n*-butyl carbinol chloride with sodium phenate, and the resulting ether is very stable and rearranges only with drastic treatment. It is extremely interesting to note that the rearrangement gives a secondary product rather than *n*-amylphenol.

Para-tertiary-amylphenol is particularly interesting industrially because its properties differ so greatly from some of those of ordinary phenol. It is not hygroscopic, is insoluble in water, and has a melting-point above 82° C. It is not as irritating to the skin as phenol and its phenol coefficient is approximately 60. When condensed with aldehydes it forms oil-soluble resins of the phenol-formaldehyde type as previously mentioned. These resins are especially suitable for use in varnishes and have the added advantage that they do not discolour on exposure to light.

When para-tertiary-amylphenol is nitrated, the dinitro derivative, in which both nitro groups appear to be in positions ortho to the hydroxyl group, is the predominating product. This arrangement would be expected since further nitration of either ortho- or para-mononitrophenol yields 2, 4-dinitrophenol and in para-tertiary-amylphenol the 4 position is already occupied by the amyl group.

During the chlorination, as described previously, the pentanes are always greatly in excess of the chlorine but, nevertheless, a small proportion of dichlorides is formed. Approximately 60% of these dichlorides are produced by direct substitution. The presence of the remaining 40% is attributed to the decomposition of tertiary chloride to trimethylethylene followed by reaction with more chlorine to form the dichloride. Since the resulting mixture does not consist entirely of dichlorides with the chlorine atoms attached to adjacent carbon atoms, the broad term 'dichloropentanes' is more appropriate than the more specific name 'amylene dichlorides'.

So many reactions are possible when these compounds are heated alone or with water or alkalies that it has been difficult to determine all of the constituents of the reaction products. High-boiling hydrocarbons with and without

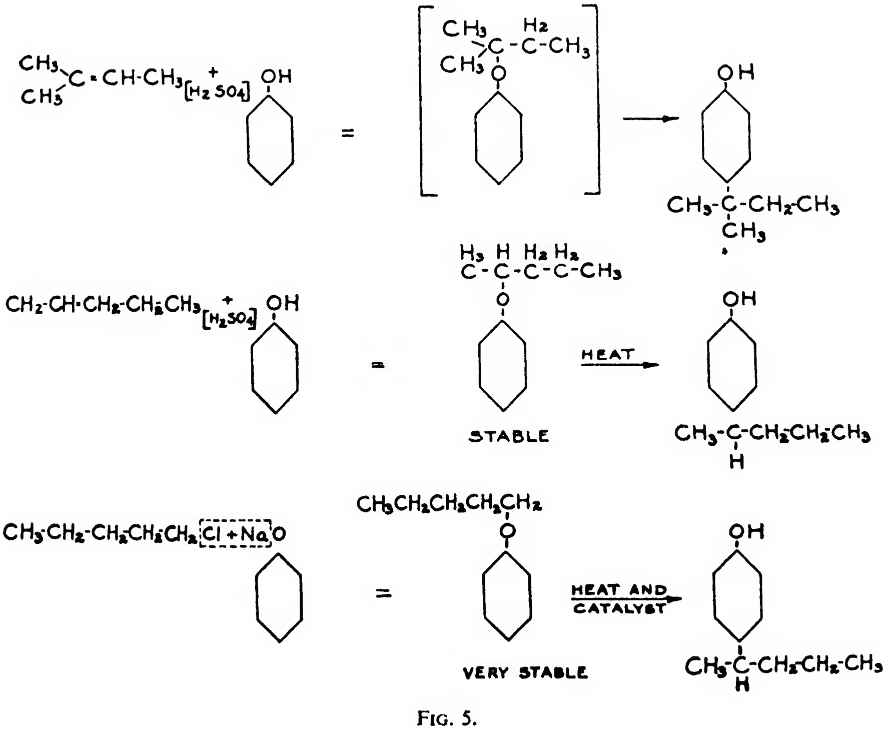


FIG. 5.

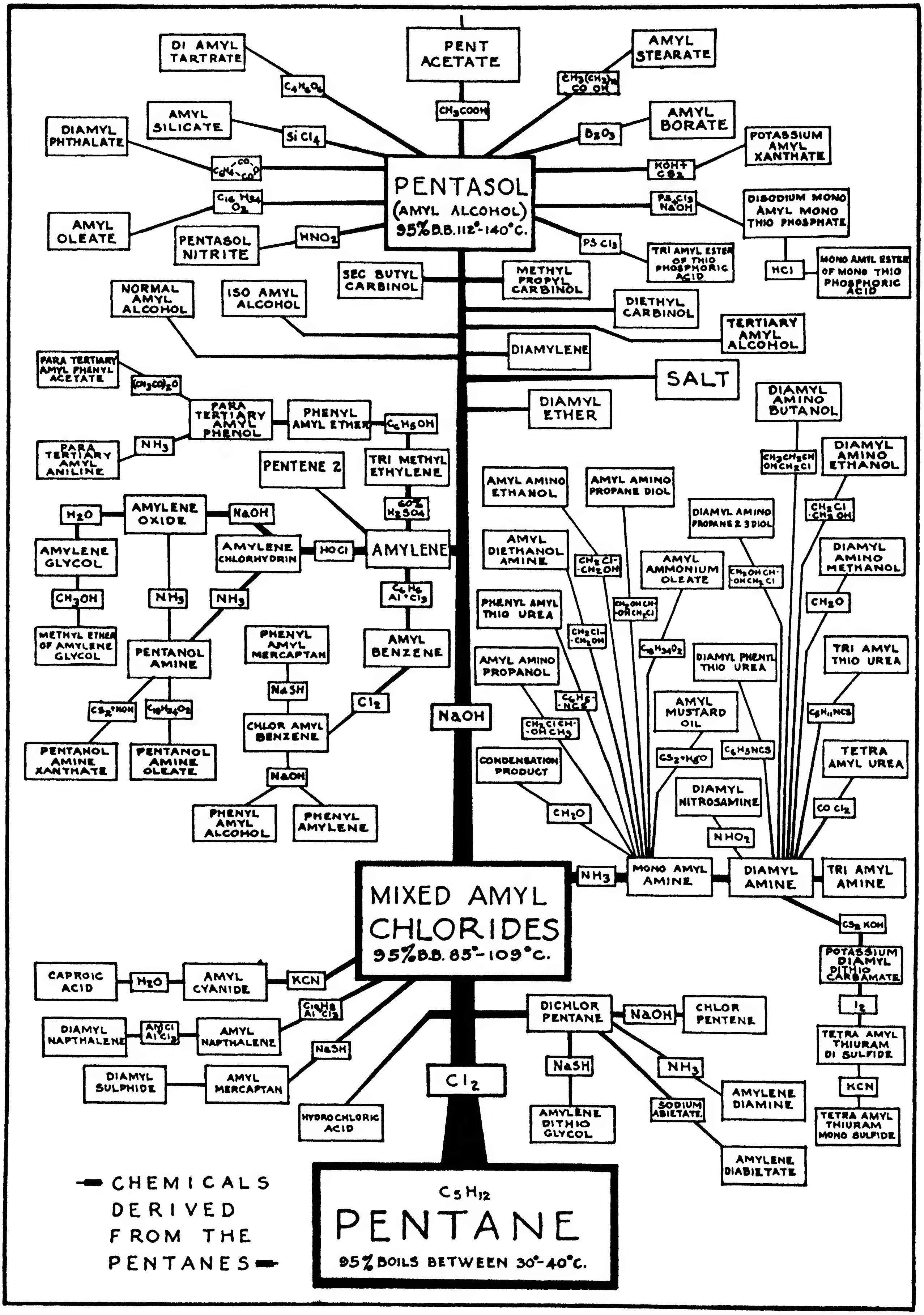

PENT ACETATE
CH_3COOH
DI AMYL TARTRATE
$C_4H_6O_6$
AMYL STEARATE
$CH_3(CH_2)_{16}CO OH$
AMYL SILICATE
$SiCl_4$
DIAMYL PHTHALATE
$C_6H_4(CO)_2O$
AMYL BORATE
B_2O_3
POTASSIUM AMYL XANTHATE
$KOH + CS_2$
PENTASOL (AMYL ALCOHOL) 95% B.B. 112°-140°C.
$C_{16}H_{34}O_2$
AMYL OLEATE
PENTASOL NITRITE
HNO_2
$PSCl_3$ $NaOH$
DISODIUM MONO AMYL MONO THIO PHOSPHATE
$PS Cl_3$
TRI AMYL ESTER OF THIO PHOSPHORIC ACID
HCl
MONO AMYL ESTER OF MONO THIO PHOSPHORIC ACID
SEC BUTYL CARBINOL
METHYL PROPYL CARBINOL
NORMAL AMYL ALCOHOL
ISO AMYL ALCOHOL
DIETHYL CARBINOL
TERTIARY AMYL ALCOHOL
DIAMYLENE
SALT
DIAMYL ETHER
PARA TERTIARY AMYL PHENYL ACETATE
$(CH_3CO)_2O$
PARA TERTIARY AMYL PHENOL
PHENYL AMYL ETHER
C_6H_5OH
NH_3
PARA TERTIARY AMYL ANILINE
PENTENE 2
TRI METHYL ETHYLENE
60% H_2SO_4
AMYLENE
$HOCl$
AMYLENE CHLORHYDRIN
AMYLENE OXIDE
$NaOH$
H_2O
AMYLENE GLYCOL
CH_3OH
METHYL ETHER OF AMYLENE GLYCOL
NH_3
NH_3
PENTANOL AMINE
$CS_2 + KOH$
$C_{18}H_{34}O_2$
PENTANOL AMINE XANTHATE
PENTANOL AMINE OLEATE
PHENYL AMYL MERCAPTAN
$NaSH$
C_6H_6 $AlCl_3$
AMYL BENZENE
Cl_2
CHLOR AMYL BENZENE
$NaOH$
PHENYL AMYL ALCOHOL
PHENYL AMYLENE
$NaOH$
DIAMYL AMINO BUTANOL
$CH_3CH_2CH OHCH_2Cl$
DIAMYL AMINO ETHANOL
$CH_2Cl \cdot CH_2OH$
AMYL AMINO ETHANOL
AMYL AMINO PROPANE DIOL
DIAMYL AMINO PROPANE 2 3 DIOL
AMYL DIETHANOL AMINE
CH_2Cl-CH_2OH
$CH_2OHCH-OHCH_2Cl$
AMYL AMMONIUM OLEATE
$CH_2OHCH-OHCH_2Cl$
DIAMYL AMINO METHANOL
CH_2O
PHENYL AMYL THIO UREA
CH_2Cl-CH_2OH
$C_{18}H_{34}O_2$
AMYL AMINO PROPANOL
DIAMYL PHENYL THIO UREA
TRI AMYL THIO UREA
C_6H_5-NCS
$CH_2ClCH-OHCH_3$
AMYL MUSTARD OIL
$C_5H_{11}NCS$
$CS_2 + HgO$
C_6H_5NCS
TETRA AMYL UREA
CONDENSATION PRODUCT
DIAMYL NITROSAMINE
$CO Cl_2$
CH_2O
HNO_2
MIXED AMYL CHLORIDES 95% B.B. 85°-109°C.
NH_3
MONO AMYL AMINE
DIAMYL AMINE
TRI AMYL AMINE
$CS_2 KOH$
POTASSIUM DIAMYL DITHIO CARBAMATE
I_2
TETRA AMYL THIURAM DI SULFIDE
KCN
TETRA AMYL THIURAM MONO SULFIDE
CAPROIC ACID
H_2O
AMYL CYANIDE
KCN
$C_{10}H_8$ $AlCl_3$
DIAMYL NAPTHALENE
$AmCl$ $AlCl_3$
AMYL NAPTHALENE
$NaSH$
DIAMYL SULPHIDE
AMYL MERCAPTAN
HYDROCHLORIC ACID
Cl_2
DICHLOR PENTANE
$NaOH$
CHLOR PENTENE
$NaSH$
NH_3
AMYLENE DITHIO GLYCOL
SODIUM ABIETATE
AMYLENE DIAMINE
AMYLENE DIABIETATE
C_5H_{12}
PENTANE
95% BOILS BETWEEN 30°-40°C.
CHEMICALS DERIVED FROM THE PENTANES

FIG. 6.

chlorine are presumably formed by the polymerization of diolefines and unsaturated monochlorides.

The dichlorides of the pentanes form constant-boiling mixtures with water, boiling between 95 and 100° C. These mixtures contain about 10 parts dichlorides to 1 part water. Distillation of 2, 3-dichloro-2-methylbutane with water is accompanied by the production of considerable hydrogen chloride, but 2, 3-dichloropentane can be distilled with water substantially without decomposition. However, it is subject to the same sort of slow hydrolysis that has been observed in carbon tetrachloride.

The dichloropentanes are splendid solvents for rubber, grease, resins, and bituminous materials. Their comparatively high flash-point (110° F.) greatly reduces the fire hazard. Because of their relatively low evaporation rate they are useful in paint and varnish removers and for the final cleaning of metal surfaces to be electroplated.

Thus, from the two pentanes (Fig. 6) a large variety of commercially important synthetic organic chemicals is being produced. Numerous other derivatives of the pentanes are made and some of these are shown in the 'Pentane Family Tree' (Fig. 6).

REFERENCES

1. Ayres, E. E. *Ind. Eng. Chem.* **21,** 899–904 (1929).
2. Bohall, H. A. *Refiner,* **11,** (8) 438 (1932).
3. Clark, L. H. *Ind. Eng. Chem.* **22,** 439–43 (1930).
4. Egloff, G., Schaad, R. E., and Lowry, C. D., Jr. *Chemical Reviews,* **8,** 1–80 (1931).
5. Ellis, C. *The Chemistry of Petroleum Derivatives.* Reinhold Publishing Corp., New York, 1934.
6. Hass, H. B. Private communications quoted by Ellis (ref. 5 above).
7. Hass, H. B., and Weber, P. *Ber.* **67** B, 974–5 (1934).
8. Weston, P. E., and Hass, H. B. *J.A.C.S.* **54,** 3337–43 (1932).

ALCOHOLS

CATALYTIC PRODUCTION OF ETHYL ALCOHOL FROM ETHYLENE

By **R. TAYLOR, M.A., B.Sc.**
Chemical Research Laboratory, D.S.I.R.

WHEN ethylene is passed into concentrated sulphuric acid the latter retains the hydrocarbon in the form of ethyl sulphuric acid, and on treating with excess of water ethyl alcohol is produced and the sulphuric acid set free. The alcohol may then be distilled off and the acid concentrated in order that it may be used afresh for absorbing more ethylene:

$$C_2H_4+H_2SO_4 = C_2H_5HSO_4$$
$$C_2H_5HSO_4+H_2O = C_2H_5OH+H_2SO_4.$$

This cyclic process in which sulphuric acid behaves as a catalyst has been known for over a century; a litre of alcohol is said to have been made from ethylene in coal gas and exhibited at the London Exhibition of 1862 (Payen [28, 1863]). It is, however, only within comparatively recent years that the process has been applied to the production of ethyl alcohol on a commercial scale. The Skinningrove Iron Company (Bury [2, 1919], Tidman [35, 1921]) developed a method for absorbing ethylene from coke-oven gas by 95% sulphuric acid heated to a temperature of 60 to 80° C., in absorption towers which were constructed so as to give a large and even turbulent surface of contact between the gas and acid, which contact lasted for about 3 minutes. The acid continued to absorb ethylene till its strength fell to 77%, when it was diluted with water to 64% sulphuric acid and distilled under 26½ in. vacuum. With an inlet gas containing 1·70% ethylene, 70 to 80% of the olefine was removed by the acid. Plant and Sidgwick [29, 1921] found that the rate of absorption of ethylene by sulphuric acid increased with temperature, but at 100° C. considerable decomposition occurred. The rate of formation of ethyl sulphuric acid was proportional to the product of the concentrations of ethylene and sulphuric acid. When the acid had absorbed about 20% of its weight of ethylene, di-ethyl sulphate was formed at a rate proportional to the product of the concentrations of ethylene and ethyl sulphuric acid. It was noted, in common with other observers, that ethyl sulphuric acid had a beneficial effect in promoting the absorption of ethylene by the acid solution.

Lebeau and Damiens [27, 1913] proposed the addition of various catalysts to promote the absorption of ethylene by sulphuric acid, and Damiens [3] has patented the use of cuprous oxide and salts for this purpose. It does not appear, however, that the addition of promoters is necessary for efficient absorption.

Ethyl alcohol is produced by the Cie Béthune (Valette [36, 1925]) in a process connected with the synthesis of ammonia; the ethylene is separated from coke-oven gas in a liquefaction process primarily intended for the production of hydrogen, and the olefine is passed under a pressure of about 20 atm. into ethyl sulphuric acid to which sulphuric acid is also added in the required amount. In this particular process the ethyl sulphuric acid is decomposed by ammonia to give ammonium sulphate and ethyl alcohol. The beneficial effect of pressure in obtaining alcohol from ethylene by means of sulphuric acid has been demonstrated by F. Strahler and F. Hachtel [33, 1934], who found that, whereas 5 kg. of sulphuric acid was necessary to obtain 1 kg. of ethyl alcohol under ordinary pressure, only 2 kg. of acid was necessary when ethylene under 15 atm. pressure was employed. The optimum temperature of absorption under pressure was 70° C.

The opinion has been expressed in the older literature that the cost of concentration of the sulphuric acid consumed would be too great for the economic manufacture of alcohol by the sulphuric acid process, but B. T. Brooks [1, 1933] considers that this aspect has been greatly changed by the manufacture of cracked gas under efficient controlled conditions, the purification of ethylene, the industrial uses for other constituents of cracked gas, the advances made in the act of concentrating sulphuric acid, and the high efficiency attendant upon the formation of large proportions of di-ethyl sulphate.

Attempts have been made to produce ethyl alcohol by passing ethylene under atmospheric and increased pressures into water in the presence of suitable catalysts. Klever and Glaser [26, 1923] found that the hydration of ethylene at 100° C. under atmospheric pressure in the presence of dilute mineral acids was a very slow reaction. In the absence of catalysts at 200° C., under 100 atm. pressure, only 0·008 g. mol. of ethylene was hydrated per g. mol. of water. Under similar conditions of temperature and pressure in the presence of 1·93% hydrochloric acid 1 g. mol. of ethylene was hydrated for every g. mol. of acid. It was concluded that even in the presence of 2 to 3% mineral acid solution the rate of hydration was too low to be of any commercial importance.

Swann, Snow, and Keyes [34, 1930] investigated the action of ethylene on water under pressures of 600 to 800 lb. per sq. in. at temperatures varying from 100 to 200° C., in the presence of 5 to 25% hydrochloric acid, and similarly hydriodic acid, also 10% hydrochloric acid plus a small amount of either aluminium chloride, cuprous chloride, bismuth chloride, or silver nitrate. The greatest concentration of alcohol obtained in any of these experiments was 0·202%, and practically no hydration occurred in the absence of a catalyst.

Patents have been taken out for such a process, involving, for example, the hydration of olefines at 150 to 250° C. under a pressure of 70 to 200 atm. with water preferably acidulated and assisted by surface action (Johannsen and Gross [30]).

Recently a large number of patents have been granted on the catalytic hydration of ethylene in the vapour phase, and it is clearly of both theoretical and practical importance that the equilibrium constant should be established for the reversible reaction:

$$C_2H_4+H_2O \text{ (vapour)} \rightleftharpoons C_2H_5OH \text{ (vapour)}.$$

This investigation was undertaken by Sanders and Dodge [31, 1934], who, in order to obtain a suitable catalyst, first studied the decomposition of ethyl alcohol under ordinary pressures. The catalysts tested included the oxide, sulphate, phosphate, phosphotungstate, silicate and chromate of aluminium, the oxide and phosphate of thorium, and tungstic acid. Aluminium oxide prepared by dissolving aluminium in caustic soda solution and then precipitating with dilute sulphuric acid, and also tungstic acid pressed into pellets with 1% powdered graphite, were selected as catalysts for the high-pressure synthesis experiments. Ethylene under pressure was first passed through a water saturator and then led over the catalyst. In certain experiments alcohol was added to the water in the saturator in order to approach the equilibrium from the decomposition side. Liquid and gaseous products were collected and analysed. In preliminary experiments at 360° C., under 135 atm. pressure, a considerable amount of oil was produced by the polymerization of ethylene, and in order to reduce this polymerization the pressure was reduced to 70 atm. in subsequent experiments. Eight runs carried out at a space velocity of 38 to 86 reciprocal hours, of both synthesis and decomposition type, were selected for calculating the equilibrium constant K_p at 380° C., and gave an average value of $1{\cdot}07\times10^{-3}$. This was compared by Sanders and Dodge with the predicted value $1{\cdot}4\times10^{-4}$ from calculation based on the free-energy change for the reaction as given by Parks and Huffman, and with the value $1{\cdot}5\times10^{-6}$ based on the entropy of ethylene calculated from the low-temperature data of Eucken and Haucks. The concentration of ethyl alcohol obtained in these experiments approached 3%.

The equilibrium constant of the vapour-phase hydration of ethylene has also been determined by Stanley, Youell, and Dymock [32, 1934] by a flow method at atmospheric pressure. The catalysts employed, with one exception, consisted of mixed acid phosphates of manganese and boron having the general composition MnO, $\frac{1}{2}B_2O_3$, xH_3PO_4, where x varied from 2·4 to 3·6. For the experiments at 145° C., the catalyst consisted of pumice impregnated with 66% sulphuric acid containing approximately 5% silver sulphate. Equilibrium constants of the system

$$C_2H_4+H_2O(g) \rightleftharpoons C_2H_5OH(g)$$

are tabulated below.

Temp.	*From synthesis*	*From decomposition*	*Mean*
145	$6{\cdot}2\times10^{-2}$	$7{\cdot}5\times10^{-2}$	$6{\cdot}3\times10^{-2}$
175	$3{\cdot}4\times10^{-2}$	$3{\cdot}8\times10^{-2}$	$3{\cdot}6\times10^{-2}$
200	$1{\cdot}59\times10^{-2}$	$1{\cdot}70\times10^{-2}$	$1{\cdot}65\times10^{-2}$
225	$1{\cdot}06\times10^{-2}$	$1{\cdot}08\times10^{-2}$	$1{\cdot}07\times10^{-2}$
250	$6{\cdot}30\times10^{-3}$	$7{\cdot}08\times10^{-3}$	$6{\cdot}7\times10^{-3}$

From these results Stanley, Youell, and Dymock obtained the following equation relating $\log_{10} K_p$ with absolute temperature (T):

$$\log_{10} K_p = (1{,}845/T)-6{\cdot}395.$$

The same authors, in order to compare their results with those of Sanders and Dodge, extrapolated their own data to 380° C., and obtained for K_p a value of $1{\cdot}06\times10^{-3}$, which in view of the great difference in the two sets of experiments shows a very remarkable agreement.

Catalysts for the vapour-phase hydration of ethylene which are detailed in the patent literature include well-recognized dehydrating catalysts, for example, sulphuric acid, phosphoric acid, and tungstic acid, as well as such substances as caustic soda and potash. The following is a list of catalysts contained in patents: sulphuric acid [5, 11, 17, 20]; sulphonic acids in aqueous solution [11]; phosphoric acid [21, 11, 14, 17]; alkali and alkaline earth metaphosphates [15, 18]; pyrophosphates [13]; acid cadmium phosphate [23]; boron phosphate [22, 8]; strontium phosphate [24]; metaphosphates of a bivalent metal [25]; phosphoric acid, uranium, iron, and cobalt [6]; phosphoric acid, copper, and manganese [7]; phosphoric acid and oxide of calcium, barium, strontium or magnesium, and also boron [10]; thoria [21]; caustic soda or potash [12]; chloride of calcium, zinc, or magnesium [16]; borax, sodium or potassium molybdate, sodium tungstate, arsenate or vanadate [19]; sodium hydrogen sulphate [4].

The Distillers Company, Ltd. [9 and 10] incorporate a drying oil such as linseed oil into certain of their catalysts during preparation of the actual material and subsequently subject the mixture to heat treatment in the presence of air. The catalyst is thus obtained in a mechanically stable form. Examples in the Distillers Company, Ltd., Patent No. 415,426, give the composition of catalysts, working conditions, and yields of ethyl alcohol in great detail, and the figures tabulated below relate to 100 c.c. of catalyst.

Example	*Composition of catalyst (g. mol.)*	*Temp. ° C.*	*Pressure atm.*	*Ethylene water vapour proportion*
1	CaO, 1·0; B_2O_3, 0·5; H_3PO_4, 3·6	280	20	2·3/1
2	,, ,,	290	40	3·0/1
3	BaO, 1·0; B_2O_3, 0·5; H_3PO_4, 3·6	280	20	2·3/1
4	,, ,,	290	40	3·0/1
5	Sr, 1·0; B_2O_3, 0·5; H_3PO_4, 3·6	290	40	3·0/1
6	MgO, 1·0; B_2O_3, 0·5; H_3PO_4, 3·6	280	30	2·3/1

Example	*Space time velocity (recip. hr.)*	*Alcohol produced (g. per hour)*	*Condensate % alcohol*	*Conversion ethylene per passage*
1	4,000	10·7	6·41	1·15
2	12,000	46·7	11·30	1·70
3	4,200	7.40	2·12	..
4	12,500	25·0	7·10	..
5	1,250	20·7	5·20	..
6	4,450	4·64	3·0	..

The temperature of reaction given in patents varies for the most part from 150 to 350° C., and the pressures specified are atmospheric or increased pressure. Increasing pressure moves the equilibrium in favour of alcohol formation, but the tendency of ethylene to polymerize under high pressure and temperature conditions brings the probable pressure of the hydration process between 1 and 100 atm.

The catalytic hydration of ethylene in the vapour phase offers certain advantages over the sulphuric acid process, but while much work has been carried out and numerous patents have been granted, the process does not yet appear to have reached the manufacturing stage.

REFERENCES

1. Brooks, B. T., *Proc. World Petr. Cong.* **2**, 840 (1933).
2. Bury, E. *Cleveland Inst. Eng. Gas J.* **148**, 718 (1919).
3. Damiens, A., *et al.* U.S.P. 1,574,796.
4. Distillers Company Ltd. B.P. 368,935.
5. —— B.P. 370,136.
6. —— B.P. 392,289.
7. —— B.P. 392,685.
8. —— B.P. 396,724.
9. —— B.P. 404,155.
10. —— B.P. 415,426.
11. Dreyfus, H. B.P. 389,133.
12. —— B.P. 389,136.
13. —— B.P. 394,375.
14. —— B.P. 394,389.
15. —— B.P. 394,674.
16. —— B.P. 396,107.
17. —— B.P. 397,187.
18. —— B.P. 407,722.
19. —— B.P. 408,304.
20. —— B.P. 409,676.
21. Imperial Chemical Industries Ltd. B.P. 308,859.
22. —— B.P. 378,865.
23. —— B.P. 369,216.
24. Imperial Chemical Industries Ltd. B.P. 407,944.
25. —— B.P. 408,313.
26. Klever, H. W., and Glaser, F. *Mitt. Chem. Tech. Inst. Tech. Hochschule Karlsruhe*, **1**, 1 (1923).
27. Lebeau, P., and Damiens, A. *Compt. rend.* **156**, 557 (1913).
28. Payen, *Dingl. Polytechn. J.* **167**, 236 (1863).
29. Plant, S. G. P., and Sidgwick, N. V. *J.S.C.I.* **40**, 14 T (1921).
30. Röchlingsche Eisen- und Stahlwerke Akt.-Ges. B.P. 238,900. See also Johannsen, O., and Gross, O., U.S.P. 1,607,459; Imperial Chemical Industries, B.P. 308,468; Dreyfus, H., B.P. 408,304; and Elkington, H. D., B.P. 335,551.
31. Sanders, F. J., and Dodge, B. F. *Ind. Eng. Chem.* **26**, 208–14 (1934).
32. Stanley, H. M., Youell, J. E., and Dymock, J. B. *J.S.C.I.* **53**, 205–208 T (1934).
33. Strahler, F., and Hachtel, F. *Brenn.-Chem.* **15**, 166–9 (1934).
34. Swann, S., Snow, R. D., and Keyes, D. B. *Ind. Eng. Chem.* **22**, 1048–51 (1930).
35. Tidman, C. F. *J.S.C.I.* **40**, 86 (1921) (cf. also Bone, W. A., *Third Report of Brit. Assoc. Committee for Investigation of Fuel Economy* (1920).
36. Valette, F. *Chim. et Ind.* **13**, 716 (1925); Cie Béthune. B.P. 221,512 (1925).

ALCOHOLS AND RELATED PRODUCTS FROM PETROLEUM OLEFINES

By BENJAMIN T. BROOKS and CARLETON ELLIS

SYNTHESIS of useful materials from petroleum and cracked gas has become an important industry during the past decade. Built upon the utilization of the bountiful supply of raw materials made available by the spread of cracking processes in gasoline manufacture, the new industry has grown primarily through development of improved methods of cracking. The separation of chemical individuals from refinery waste gases has allowed products to be obtained in a high state of purity. Even as cheap a solvent as ethyl alcohol fermented from molasses has felt competition from the synthetic product from ethylene, and numerous other synthetics were never available commercially before.

In the following account much of the earlier academic work, as well as many of the patents in this field, must be omitted. A more detailed survey of the earlier literature and patents, up to 1934, has been given by Ellis [19, 1934].

Most of the important developments so far undertaken in this field have been fitted into existing refinery operations. One company producing a series of alcohols and related derivatives utilizes the by-product still gases produced by a pressure cracking operation. Another company produces ethylene glycol and ethyl alcohol from the by-product gas of a vapour-phase cracking plant. Thus the utilization of uncondensed cracked gases, formed incidentally in cracking for gasoline (the principal product), bears the same economic relation to petroleum refining as the manufacture of coal-tar light oil and its derivatives does to the coking of coal.

Synthetic ethyl ether was made on a small commercial scale at Richmond, Va., in 1896 by Fritzsche [26, 1897, 1898]. The commercial introduction of oil cracking processes in 1912 may be said greatly to have stimulated petroleum research and opened the way for the present development of petroleum synthetics, since the refining of cracked gasoline and the utilization of the *by-product* cracked gas presented new problems which later developed into the present industry. Application of the standard method of refining by sulphuric acid to the treatment of cracked gasoline containing 30% or more of olefines gave an acid extract from which an oil separated on dilution. In a study of this problem in 1918, Brooks and Humphrey [10, 1930] showed that this acid oil contained secondary and tertiary alcohols, and the investigation was extended to a number of pure amylenes, hexenes, and other olefines. Ellis and Cohen [23, 1924] suggested that acid more dilute than the customary 66° Bé. (1·87 sp. gr.) be used for refining cracked gasoline, thus reducing the loss by polymerization. The first production of alcohols industrially from oil gas and cracked gasoline was made by Ellis and his co-workers [21, 1920]. The development of synthetic ethyl alcohol in Europe, beginning about 1919, was focused on the utilization of the ethylene in coal gas in the plant of the Skinningrove Iron Company in England, and at Bethune in France.

Manufacture, Separation, and Purification of the Olefines

Although oil gas has long been known, its production at low cost was hardly possible prior to the development of vapour-phase or high-temperature cracking processes in recent years. The old Pintsch gas retorts were very inefficient and were operated over a wide temperature range. Close temperature regulation, particularly in high-temperature cracking, was appreciated by W. A. Hall, one of the pioneers of oil cracking, and this feature was greatly improved by Luis de Florez, inventor of a cracking process adapted to vapour-phase operation. During the World War the Hall process was operated at high temperatures for the conversion of petroleum to benzene and toluene. In the Hall process cracking at 605° C. (1,120° F.) gave 17·7% gas containing 49 to 50% olefines; at 725° C. (1,337° F.) 66% of the oil was gasified, the gas containing 40% total olefines [4, 1926].

It has long been known that the olefines are unstable at the temperatures employed to produce them by cracking. This was particularly pointed out by Whitaker and Rittman [50, 1914] and Whitaker and Alexander [49, 1915]. Also in more recent work by Frey and his associates [25, 1932] it is shown that when propane and butane are cracked to produce a maximum of olefines—i.e. at about 850° C. (1,560° F.)—an exothermic reaction quickly ensues, a further temperature rise of 94° C. (201° F.) having been observed. During this exothermic period benzene and other condensable hydrocarbons are formed and the yield of olefines is considerably decreased. Most of the research and development in this field of high-temperature cracking of the simple paraffins, methane to butane inclusive, has been carried out with the object of producing benzene or for the purpose of enriching lean gas such as water gas. This subject and the pyrolysis of individual hydrocarbons have recently been reviewed by Ellis [20, 1934].

Owing to the potentially enormous quantities of propane and butane which are available as by-products of the stabilization of gasoline, the cracking of propane and butane to produce gaseous olefines has industrial promise. Podbielniak and others have obtained a maximum ethylene yield at about 815° C. (1,500° F.) from commercial propane. One volume of commercial propane, in the form of stabilizer overhead, gave about 1·8 vol. of cracked gas containing 26 to 28% ethylene. The results of Podbielniak are of significance since they were obtained on an industrial unit scale. Stabilizer gas produced at large refineries or by gasoline recovery plants situated on large gas transmission lines are the most permanent sources of supply.

Much of the published data with respect to yields of oil gas by cracking at particular temperatures is of very little value; many important factors are usually neglected, such as time of passage, diameter of heating tubes, ratio of recycled oil to fresh charging stock, nature of the charging stock, &c. None of the older results gives analyses showing the percentages of the individual olefines. The figures from the literature [4, 1926] do show, however, the rapidly increasing gas yields as the temperature is increased (Table I).

So many factors are changed when small-scale experimental operations are enlarged to commercial unit operations that it is not safe to base projected commercial operations on small-scale results.

TABLE I

Yields of Olefines by Cracking

No.	Temp. °C.	Temp. °F.	Gas per 42 U.S. gal. of oil cu. ft.	Olefines %	Remarks
1	593	(1,099)	1,260	45–8	Gyro gasoline manufacture
2	650	(1 202)	1,887	43·6	Experimental
3	682	(1,260)	2,490	35·8	Pa. gas oil
4	700	(1,292)	2,520	36·5	Russian gas oil
5	743	(1,369)	2,990	36·6	Experimental
6	743	(1,369)	3,136	33·5	"
7	750	(1,382)	2,884	30·6	"
8	760	(1,400)	2,968	30·1	Pa. gas oil
9	782	(1,440)	3,365	27·7	Experimental
10	800	(1,472)	2,870	46·2	Experimental. Oil 0·847
11	850	(1,562)	3,255	43·1	Experimental. Oil 0·807

Some of the earlier results, reported by Wagner [47, 1935] for commercial vapour-phase cracking showed 30% or more of the charging stock converted to wet gas. Gas formation has since been reduced in the Gyro operations. Gas from one of these plants in 1931 showed the following analyses:

TABLE II

Composition of Gas by Vapour-phase Cracking

(% by vol.)

	I	*II*
CO_2+H_2S	0·89	0·28
CH_4+H_2	29·6	28·5
Ethylene	23·1	23·1
Ethane	13·3	15·7
Propane	4·9	4·4
Butenes and butane	8·3	10·1
C_5	4·1	4·0
Above C_5	3·9	3·1
Total olefines	47·2	48·4

The following results recently obtained on a small-size vapour-phase unit are of interest as showing that in cracking in the temperature range 580 to 610° C. (1,075 to 1,130° F.) the composition of the pentane-free gas remains very little changed when the rate of feed is increased with increasing cracking temperature, thus decreasing the time of passage through the cracking zone. When the feed rate is kept constant with increasing cracking temperatures, the yield of gas is greater. The higher gas yields necessarily result from cracking of gasoline, which at least for most purposes is uneconomical.

TABLE III

Yields and Composition of Gas and Gasoline by Cracking East Texas Reduced Crude at Atmospheric Pressure

Cracking temp., ° C. (° F.)	*580 (1,075)*	*600 (1,110)*	*610 (1,130)*
Pentane-free gas:			
Wt. % of feed	22·5	24·9	26·5
Cu. ft. per bbl. of feed	855	990	1,025
Cu. ft. per bbl. gas oil	1,125	1,300	1,350
Composition, vol. %:			
Methane and hydrogen	27·4	32·5	30·5
Ethylene	22·2	23·9	23·4
Ethane	14·4	13·4	12·4
Propylene	19·8	16·8	19·0
Propane	6·9	4·9	5·6
C_4 hydrocarbons	9·2	8·5	9·0
Gasoline, 9·6 lb. Reid vapour pressure, 400° F. end-point:			
Vol. % of feed	41·9	40·0	34·1
Vol. % of gas oil	55·1	52·6	44·9
° API.	58·9	58·0	57·0
Gasoline composition, vol. %:			
Butenes	5·9	6·3	6·0
Butanes	2·1	2·3	2·2
Pentenes	7·7	7·4	9·0
Pentanes	5·8	4·5	4·9
C_6 hydrocarbons	15·7	16·1	17·1
C_7 hydrocarbons plus	62·8	63·4	60·7

The East Texas crude (26·1° API. gravity) represented 60% of the original crude and contained about 24% residual fuel oil not volatilized in the apparatus.

The figures in Table III were obtained by analyses of the dry residual gas, the stabilizer overhead product, mainly consisting of three- and four-carbon atom hydrocarbons, and the stabilized end-point gasoline.

Similar results have been reported by Geniesse and Reuter [27, 1932], who cracked Mid-Continent gas oil in a small experimental apparatus. The ethylene content of the gas was found to be nearly constant through the temperature range 600 to 640° C. (1,110 to 1,185° F.), the time of cracking being decreased as the temperature was increased.

Composition of Olefine-Paraffin Fractions

In the treatment of cracked gases, it is usually not feasible or particularly desirable to separate the olefines from the corresponding paraffins.

In the case of ethylene-ethane (the gas made by industrial vapour-phase cracking at 595° C. (1,103° F.) noted in Table II) the ratio of ethylene to ethane is 100 to 51. In the experimental-scale results given in Table III these ratios are as follows:

Cracking temp., ° C. (° F.)	580 (1,076)	600 (1,112)	610 (1,130)
Ethylene-ethane ratio	100/65	100/56	100/53

The propylene-propane ratios are as follows:

Cracking temp., ° C. (° F.)	595 (1,103)*	580 (1,076)	600 (1,112)	610 (1,130)
Propylene-propane ratio	100/32	100/35	100/29	100/29

*Large scale.

The material used industrially for the manufacture of *iso*-propyl alcohol is the overhead gas produced when stabilizing cracked gasoline, made by pressure cracking, and contains approximately 18% propylene.

The butene fraction separated on an industrial scale from gas produced by vapour-phase cracking contained the following:

	%		%
Butanes	10–12	Butadiene	12–14
iso-Butene	20–4	C_3 and C_5	2·0
n-Butenes	50–5		

Other types of oil gas contain these same hydrocarbons in varying amounts, the gases made by cracking at lower temperatures and under pressure containing much more butane and little or no butadiene. A four-carbon fraction made by the Cross cracking process showed 22% butenes and no butadiene.

Of the normal butenes present, 2-butene predominates. The initial product is doubtless 1-butene, which is rearranged to 2-butene. The butenes made by small-scale experimental cracking, where the cracking time is very short, yield larger proportions of 1-butene. The relative proportion of 1-butene is of considerable importance for certain synthetic applications, though both yield 2-butanol exclusively in the sulphuric acid-alcohol method.

The pentene-pentane fraction made by large-scale vapour-phase cracking contains 18 to 25% pentanes; the product of the small-scale fraction contains a larger proportion of pentanes. The pentene-pentane fraction, made by pressure cracking for gasoline, contains 25 to 33% pentenes, depending upon the temperatures and possibly the time-factor in the cracking process employed.

The 'amylene' reported in the early literature usually referred to amylene made by the decomposition of amyl alcohol or fusel oil and contained large proportions of trimethyl ethylene; accordingly it was reported to yield chiefly *tert*-amyl alcohol when treated with sulphuric acid under suitable conditions.

The pentene-pentane fraction contains 1-pentene, 2-pentene, trimethyl ethylene, *iso*-propyl ethylene, probably *asym*-methyl ethyl ethylene, and only very small proportions (about 1%) of dienes. Also the proportion of pentenes yielding *tert*-amyl alcohol (2 to 4% in material of vapour-phase origin) is much smaller than the *iso*-butene content of the butene fraction. *Iso*-propyl ethylene appears to be one of the constituents of the pentenes produced by either vapour-phase or pressure cracking.

The composition of the hexene-hexane fraction, made by vapour-phase or by pressure cracking, is not known. The alcohols made from this fraction are derived from the normal hexenes.

Concentration and Purification of Olefines

For most chemical reactions, as for example absorption in sulphuric acid, there are obvious advantages in using gas rich in olefines. Since in the earlier work on the manufacture of ethyl alcohol from ethylene, coal gas was employed, many methods of concentrating the ethylene were tried. Bury and Ollander [11, 1919] tried the method of partially selective adsorption by charcoal, patented by Soddy [41, 1925], but abandoned it. Berl and Schmidt [3, 1923] have reported quantitative experiments with this method.

The process of Claude, primarily directed to the purification of the hydrogen of coal gas, liquefies the ethylene and a portion of the methane at −140° C. (−220° F.). This method was tried at Bethune, France, and a fraction was obtained containing 20 to 30% of ethylene [45, 1925]. The Société Anonyme d'Explosifs [40, 1925] employed both pressure and cooling to separate a series of hydrocarbon fractions, and a liquid ethylene-ethane fraction. Absorption in a hydrocarbon oil, followed by rectification in the presence of the solvent oil, has been patented by Curme [14, 1922], and Voorhees and Youtz [46, 1932] concentrate ethylene by utilizing its greater solubility, as compared with methane and ethane, in ethyl alcohol under pressure. Joshua and Stanley [29, 1935] have shown that ethylene may be concentrated from lean oil gases by absorption under pressure in aqueous solutions containing cuprous chloride and ethanolamine, a labile compound being formed. Ethylene is liberated on releasing the pressure and warming. Ethylene homologues also react with this reagent, but apparently not as readily as ethylene.

Bury and Ollander found that with reasonably good surface contact between the acid and the gas 71% of the 2·5% ethylene originally present in the coal gas could be absorbed in 2 min. by 95% sulphuric acid at 60 to 80° C. (140 to 175° F.). Tideman reported that 80 to 90% of the ethylene was absorbed under the same conditions in 3 min.

In his early work Fritzsche [26, 1897, 1898] removed the ethylene homologues from oil gas by the action of concentrated sulphuric acid at temperatures below 40° C. (104° F.). Ellis [22, 1923] described the removal of propylene by treating with sulphuric acid of specific gravity 1·8 at low temperatures, followed by reaction of the ethylene with more concentrated acid above 60° C. Isham and Born [28, 1929, 1930] and Taveau [43, 1932] have described similar methods of successively removing butenes, propylene, and ethylene.

It has long been known that *iso*-butene is much more reactive to dilute mineral acid than the normal butenes, readily yielding *tert*-butyl alcohol, and that trimethyl ethylene is much more reactive than the normal pentenes and may be selectively removed from the olefine mixtures containing the isomeric pentenes. The relative reaction rates of these olefines with sulphuric acid have been reported by Davis and Schuler [16, 1930]. These reaction rates are so different that the separation of the olefine-yielding tertiary alcohols from the normal butenes and pentenes, which yield secondary alcohols, has been carried out industrially. Hydrochloric acid has been proposed for the same purpose but has not been thus used industrially.

It was early recognized that hydrogen sulphide and mercaptans should be removed, or the resulting alcohols, made by reaction with sulphuric acid, contain mercaptans.

Selective removal of butadiene from the butene fraction, made by vapour-phase cracking, is advantageous to the butyl-alcohol process, as will be noted later. It can be selectively removed by cuprous chloride.

General Considerations

In the following discussion only the processes based upon solution of olefines in acid, followed by hydrolysis, are considered. Although the chemistry of the processes is relatively simple, synthetic alcohols have been made in this way only since the World War.

Sulphuric acid is now the only reagent used industrially for the conversion of olefines to alcohols. Other reagents of an acid character have been proposed, but for various reasons (mostly poorer yields) they are not used.

Probably in all cases the acid reagents first combine with the olefines to form definite chemical compounds which are simultaneously, or more often later, hydrolysed to give alcohols. In an effort to avoid the use of more or less concentrated sulphuric acid, a number of processes have been proposed which describe the hydration of the olefine (ethylene) as 'catalytic' or 'direct'; most of these processes employ a dilute acid or an acid salt, usually with steam under high pressures. It seems more consistent with all of the known facts to suppose that in such processes the function of the acid reagent is initially the same as in the more familiar reactions with concentrated acid, i.e. compound formation followed by hydrolysis.

Anhydrous or 100% sulphuric acid causes carbonization even with ethylene, and temperature control is difficult. The function of the water in less concentrated acid is more than that of a mere diluent. In the concentrations commonly employed for secondary hexyl, amyl, butyl, and *iso*-propyl alcohols, the reagent chiefly used is the hydrate $H_2SO_4 \cdot H_2O$; the equilibrium

$$H_2SO_4 + H_2O \leftrightarrows H_2SO_4 \cdot H_2O$$

is generally believed to exist in acid corresponding to this composition. The stability of the substance $H_2SO_4 \cdot H_2O$ is indicated by its large heat of formation, which is also consistent with the fact that, when this so-called hydrate reacts with an olefine, the alkyl sulphate $ROSO_3H \cdot H_2O$

is formed without loss of water, as is indicated by the composition of a large number of salts, such as $Ba(OSO_3C_2H_5)_2 \cdot 2H_2O$. Also, when a solution containing 85% sulphuric acid reacts with an olefine there is no decrease in the reaction rate as the reaction proceeds, proving that there is no increase in the proportion of water to uncombined acid. When dialkyl sulphates are formed by the reaction of a monoalkyl sulphate ($RSO_3H \cdot H_2O$) with an olefine, the resulting dialkyl sulphate, $(RO)_2SO_2$, is anhydrous; this may explain the fact that the sensible heat of reaction is very small compared with that of forming the monosulphate, and that, when using 90 to 96% sulphuric acid, equilibria are reached in forming the dialkyl sulphate, caused by the liberation of water,

$$ROSO_3H \cdot H_2O + R\ (\text{olefine}) \rightarrow (RO)_2SO_2 + H_2O.$$

Dialkyl Sulphate Formation. The formation of mono- and dialkyl sulphates proceeds simultaneously. For example,

$$CH_2{:}CH_2 + H_2SO_4 \cdot H_2O \rightarrow C_2H_5OSO_3H \cdot H_2O,$$
$$C_2H_5OSO_3H \cdot H_2O + CH_2{:}CH_2 \rightarrow (C_2H_5O)_2SO_2 + H_2O.$$

In the case of ethylene, appreciable amounts of diethyl sulphate are formed when the acid has reacted with about one-third mol. [37, 1921]. This has the result that, on treating a cracked naphtha or a mixture of olefines and paraffins, part of the dialkyl sulphate formed passes into the residual naphtha, usually requiring redistillation of the residual naphtha before blending with gasoline. The higher dialkyl sulphates (dibutyl and diamyl sulphates, &c.) are miscible with hydrocarbon solvents, and gasoline, refined by treating with concentrated sulphuric acid, always contains dialkyl sulphates which are decomposed on redistilling [10, 1930].

Large yields of dialkyl sulphate are favoured by the solution of excess olefine in the monoalkyl sulphate-acid mixture which, in the case of ethylene, is readily affected by pressure (Fig. 2). In the case of the pentenes the excess of olefine is readily soluble in the monoalkyl sulphate-acid mixture and reacts readily at 20° C. (68° F.) to form large yields of diamyl sulphate.

Dialkyl sulphates are also formed by the following type of reaction:

$$2C_2H_5OSO_3H \rightleftharpoons (C_2H_5O)_2SO_2 + H_2SO_4,$$

which reaction, in fact, has been a well-known method of preparing diethyl sulphate; on heating ethyl sulphuric acid under vacuum, diethyl sulphate is distilled from the mixture.

Polymer Formation. The formation of polymers,

$$xC_5H_{10} \rightarrow C_{10}H_{20} + C_{15}H_{30},\ \&c.,$$

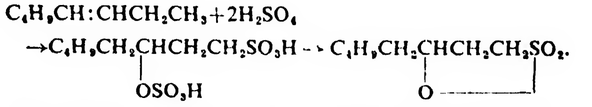
is insignificant in the case of ethylene at temperatures below 80° C. (176° F.) and acid concentrations below 96%. With higher temperatures and more concentrated acid, secondary reactions, decomposition, carbonization, and formation of sulphur dioxide and tar are noted. Polymerization of propylene and the higher olefine homologues may be a serious loss if the conditions of acid concentration and temperature are too severe. The reason for increasing polymer formation with increasing acid concentration is not known. In a mixture of olefines one olefine may polymerize and couple with it another olefine which by itself is not polymerized. Thus, when butadiene is polymerized by 75% sulphuric acid in the presence of normal butenes, viscous high-boiling polymers are formed in about double the proportions of the butadiene present. Thomas and Carmody [44, 1932] have noted similar co-polymerization when mixtures of olefines and dienes are polymerized by anhydrous aluminium chloride.

The most interesting of the various theories of polymerization which has been proposed is that of Whitmore [51, 1933], which is based upon modern theories of organic reactions. Whitmore's theory was suggested as applying only to polymerization of olefines by acids and takes no account of the polymerizations by anhydrous reagents (alkali metals such as sodium and potassium, fuller's earth, and similar adsorbents) or by heat and pressure alone.

Formation of Saturated Hydrocarbons. In concentrated sulphuric acid, in addition to polymerization, Ormandy and Craven [36, 1928] and Nametkin and Abakumovskaja [35, 1933] have shown that saturated hydrocarbons are formed. Whereas cyclohexene gives good yields of cyclohexanol with 80 to 85% sulphuric acid, concentrated sulphuric acid yields two saturated hydrocarbons, $C_{12}H_{22}$ and $C_{18}H_{32}$. No satisfactory theory has as yet been advanced for these results:

$$xC_6H_{10}\ (\text{cyclohexane}) \rightarrow C_{12}H_{22} + C_{18}H_{32} + (?)$$

Sulphone and Carbyl Sulphate Formation. Carbyl sulphate is not known to be formed by the reaction of ethylene and sulphuric acid of less than 100% strength. With ethylene homologues similar anhydrides are apparently formed more readily with moderately concentrated acids, as is indicated by the isolation of octane sulphone by Baldeschwieler and Cassar [2, 1929] from the residual polymers made in the alcohol plant of the Standard Alcohol Company. They give the following reactions for its formation:



$$C_4H_9CH{:}CHCH_2CH_3 + 2H_2SO_4$$
$$\rightarrow C_4H_9CH_2\underset{\substack{|\\ OSO_3H}}{C}HCH_2CH_2SO_3H \dashrightarrow C_4H_9CH_2\underset{\substack{|\\ O}}{C}HCH_2CH_2SO_2.$$

The formation of carbon on concentrating the diluted sulphuric acid used in alcohol manufacture is in all probability due to sulphonic derivatives of the unhydrolysable isethionic acid type:

$$SO_3HCH_2CH_2OSO_3H + H_2O \leftrightharpoons SO_3HCH_2CH_2OH + H_2SO_4.$$

Hydrolysis of Alkyl Sulphates. Alkyl sulphates are fairly stable in the presence of water at ordinary temperatures. On heating with water, they are readily hydrolysed and this hydrolysis is promoted by hydrogen ions. The effect of excess sulphuric acid on the hydrolysis of alkyl sulphates in the diluted acid product obtained in large-scale practice is very marked, being more rapid when excess free sulphuric acid is present. The monoalkyl sulphates are most stable in excess caustic alkali solution and may be boiled in such solutions with only very slow hydrolysis, but in acid solution the hydrolysis is increasingly rapid with increasing acid concentration, as shown in Figs. 3 and 4. This behaviour is in accord with the observations of Drushel and Linhart [18, 1911] on the effect of hydrochloric acid on the hydrolysis of barium ethyl sulphate, but contrary to the generalization as to the hydrolysis of such esters in acid and alkaline solution given by Rice [38, 1928].

In moderately concentrated acid solutions the following equilibria may be assumed:

$$ROSO_3H + H_2O \leftrightharpoons ROH + H_2SO_4,$$
$$(RO)_2SO_2 + H_2O \leftrightharpoons ROSO_3H + ROH.$$

These equilibria have not been investigated, with the exception of the reaction of ethyl alcohol and sulphuric acid. It is sometimes considered desirable to minimize reversion to olefine by hydrolysing the alkyl sulphates prior to distillation [34, 1922, 1933]. The hydrolysis of the dialkyl sulphates is complicated by ether formation.

Ether Formation. In the manufacture of butyl and amyl alcohols the sulphating reaction is usually not carried beyond the formation of the monoalkyl sulphate, and ether formation is not appreciable. In the case of ethyl and *iso*-propyl alcohols, the dialkyl sulphates are more readily formed; when the acid reaction product, containing disulphates, is diluted, hydrolysed, and distilled, ethers are formed. These ethers are produced mainly by the reaction of the dialkyl sulphates with alcohol:

$$(C_2H_5O)_2SO_2 + C_2H_5OH \rightarrow (C_2H_5)_2O + C_2H_5OSO_3H.$$

Thus ethyl alcohol may be distilled from a 40% solution of sulphuric acid without appreciable ether formation, but, when diethyl sulphate is added to such a mixture, as much as 32% of the diethyl sulphate is converted to ethyl ether. The formation of ethyl ether in this way can be minimized by separating the diethyl sulphate from the acid-reaction product and hydrolysing it separately with water or dilute acid, with vigorous agitation, or by adding the ester gradually to boiling water in which the concentration of alcohol is kept low by distilling the alcohol as fast as it is formed.

Ethyl ether and di-*iso*-propyl ether are available in large quantities as by-products of the manufacture of synthetic alcohols.

Decomposition of Alkyl Sulphates. The decomposition of alkyl sulphates by heating is a well-known method of preparation of the simple olefines. Except in the case of ethyl alcohol, rather dilute sulphuric acid (50% or less) is used for this purpose. In the case of ethyl and *iso*-propyl alkyl sulphates, hydrolysis and distillation may be carried out in solutions of 35% sulphuric acid without appreciable decomposition to olefines. In the case of butyl, amyl, and hexyl alcohols decomposition of the alkyl sulphates to olefines is an important factor in industrial operations.

The dialkyl sulphates carbonize on decomposition by heat, giving sulphur dioxide and small yields of olefines. As shown by Nef, no ether is formed by the decomposition of diethyl sulphate by heat. The dialkyl sulphates are stable at the low temperatures at which they are formed; when dissolved in neutral hydrocarbon oil, rapid decomposition is noted at 140 to 150° C. (284 to 302° F.).

Ethyl and *iso*-Propyl Alcohols

Synthetic ethyl ether was made on a small industrial scale in Richmond, Va., from the ethylene in oil gas by Fritzsche [26, 1897, 1898] in 1896. Apparently no attempt was made to utilize any of the ethylene homologues in the oil gas, since they were polymerized by the concentrated sulphuric acid used. Although Fritzsche reported a yield of ether equivalent to 70%, based on the ethylene in the gas, his acid consumption was high. The entire cost of the operation was borne by the single product made. The results of Fritzsche have led many writers to condemn the economics of synthetic ethyl alcohol. Fritzsche recovered only about one-third of the sulphuric acid used, much of this loss resulting from polymerization and tar formation from the ethylene homologues removed in the preliminary acid-scrubbing of the gas, and also decomposition of the acid during subsequent reconcentration. His acid efficiency was also very low because, although he used 98% acid at 80° C. (176° F.) for absorbing the ethylene, the reaction was not carried beyond 0·64 mol. of ethylene per mol. of sulphuric acid.

The chief factors which have changed the picture altogether with regard to commercial synthetic ethyl alcohol are the following. The development of efficient methods of removing butenes and propylene by sulphuric acid to produce butyl and *iso*-propyl alcohol, on the one hand, and the development of physical methods of separating ethylene and propylene, make it feasible to produce synthetic ethyl alcohol of very high purity. The absorption of ethylene by sulphuric acid is more rapid when the acid contains ethyl sulphuric acid, as was noted by Fritzsche and later by Plant and Sidgwick and by Cie Bethune [37, 1921; 13, 1925]. What is still more important, the absorption of ethylene proceeds to form substantial proportions of diethyl sulphate, which greatly reduces the acid requirement as compared with the practice of Fritzsche or the Skinningrove Iron Company. Curme [15, 1920] proposed to make diethyl sulphate commercially in this way, using pure ethylene and volatilizing the diethyl sulphate from the acid mixture in a stream of excess gas. Plant and Sidgwick also noted the formation of diethyl sulphate, and Maimeri [32, 1924] claimed its production by absorbing ethylene in concentrated acid at 65 to 75° C. (149 to 167° F.) under low pressure and diluting the acid product to precipitate the diethyl sulphate. Finally, the absorption of the ethylene is greatly accelerated by the use of pressure [6, 1932, 1933; 8, 1934]. The rate of absorption of the ethylene, using 95% acid at 80 to 90° C. (176 to 194° F.), shows very little falling off until 1·5 mols. of ethylene are absorbed per mol. of sulphuric acid, or more than double the absorption attained by Fritzsche. The use of pressures within the range of 250 to 500 lb. per sq. in. are particularly convenient when the propylene and higher boiling hydrocarbons are separated by fractionation or oil absorption under pressure. The use of pressures of this order also prevents vaporization loss of diethyl sulphate from rich acid reaction mixtures. An experimental investigation of the absorption of ethylene by sulphuric acid, under pressures up to 20 atm., has recently been published by Strahler and Hachtel [42, 1934].

The rate of absorption of ethylene by the acid depends very largely on the surface contact of the acid and the gas, and agitation of the acid.

The use of catalysts to promote the reaction of ethylene and sulphuric acid has frequently been proposed. Silver and mercury salts have a substantial catalytic effect on this reaction. The patent literature is summarized by Ellis [19, 1934]. However, the use of catalysts of this nature may present some difficulties in large-scale operation and they would probably be lost in the process of acid recovery. The advantages appear to be of doubtful value in view of the rapid reaction with concentrated sulphuric acid at about 80° C. (176° F.) when carried out under pressures of 300 to 500 lb. per sq. in.

The use of a wide range of dilutions of various mineral acids, at high temperatures and pressures, has been proposed, but none of these processes appear to be in industrial use at the present time. The Distillers Co., Ltd. [17, 1932, 1934], describe passing a mixture of ethylene and steam through sulphuric acid of 60 to 85% at temperatures up to 200° C. (392° F.). Other processes claim the reaction of ethylene with very dilute acids at temperatures of 150 to 250° C. (302 to 482° F.) and pressures of 70 to 200 atm., and in the presence of silver or copper salts as catalysts [19, 1934].

The first account of the manufacture of *iso*-propyl alcohol from cracking-still gas was published in 1920 by Ellis [21, 1920]. A gas richer in propylene than cracking-still gas and substantially free from butenes, obtained as stabilizer overhead gas, is now employed. This gas, containing 16 to 18% propylene, is treated with sulphuric acid in a steel tower provided with cooling coils and in the presence of an absorbent oil as shown in the patents to Lebo [31, 1932] and Mann and Williams [33, 1921]. At low operating pressures the use of absorbent mineral oil greatly increases the capacity of the reaction tower. The absorption is normally carried out until the acid reaction product contains a substantial proportion of di-*iso*-propyl sulphate. After separating the neutral oil and acid product, the latter is hydrolysed and distilled continuously with steam. On rectifying the crude *iso*-propyl alcohol, *iso*-propyl ether is obtained in the lower boiling fraction.

The liquefied propylene-propane fraction, derived from the products of vapour-phase cracking, may contain as much as 80% propylene, the remainder being propane, and because this is in the liquid condition it may be agitated with acid for any length of time desired, and it is possible to carry out the reaction with sulphuric acid of 80 to 85% strength. When carried out under pressure at 15 to 20° C. (59 to 68° F.) using 85 % acid, the product is largely di-*iso*-propyl sulphate and the formation of polymers is almost entirely avoided.

Secondary Butyl, Amyl, and Hexyl Alcohols. As already noted, the butene fraction contains *iso*-butene and the normal butenes, the pentene fraction contains the two normal pentenes and also *iso*-propylethylene and trimethylethylene, and the hexene fraction contains a mixture of hexenes which have not been identified except indirectly from the alcohols made from them.

Tertiary butyl alcohol was prepared from *iso*-butene by Butlerow [12, 1867, 1875, 1880] by the action of dilute sulphuric acid. The relative reaction rates of the butenes with sulphuric acid of various concentrations has been reported by Davis and Schuler [16, 1930] from which the selective removal of *iso*-butene from a mixture of butenes by 65% sulphuric acid will readily be understood. The literature notes that *tert*-butyl alcohol is decomposed on warming with mineral acids as dilute as 0·02 normal, and early in this development it was thought necessary to neutralize the diluted acid product to obtain the tertiary alcohols. However, by rapid continuous distillation in a column with steam, it has been found possible to recover 80% of the *tert*-butyl alcohol present from acid solutions containing 35 to 40% sulphuric acid.

The *iso*-butene polymers, useful as solvents, as high-octane motor fuel, and for other purposes, can be recovered in good yields by heating the 65% acid solution. Di-*iso*-butene is readily hydrogenated in the presence of nickel catalysts to the corresponding octane, and this is the only source of this well-known motor-fuel standard.

The butadiene content of the butene fraction, derived from vapour-phase cracking, is ordinarily 12 to 14%, and the butadiene yield cannot be materially increased except by cracking at higher temperatures and sacrificing the yields of gasoline and other products. It is not probable that this interesting material will be available for synthetic rubber or other chemical syntheses, except as a by-product of the utilization of the gases and light olefines made by vapour-phase cracking. Butadiene has been isolated from this fraction on a small-plant scale by means of its solid double compound with cuprous chloride. The butene fraction was agitated with a thin slurry of cuprous chloride in a 10% solution of ammonium chloride in a copper-lined vessel [5, 1932]. The butenes and butane were then allowed to boil off, and condensed under a few pounds pressure, and the double compound was then decomposed by heating to 55 to 60° C. (131 to 140° F.). Although the cuprous chloride was found to react slowly with *iso*-butene, the formation of the insoluble butadiene compound was so rapid as to be nearly quantitative and very selective.

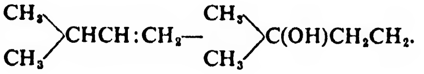
It was found that, contrary to statements in the patent literature, *iso*-butene could be selectively removed by 65% sulphuric acid at 10 to 15° C. (50 to 59° F.) without polymerizing the butadiene.

If not removed, butadiene is completely polymerized by the more concentrated acid employed to react with the normal butenes. The resulting polymerization includes approximately 1 mol. of normal butene to one of butadiene, to yield a high-boiling oil having iodine absorption numbers (Hanus method) as high as 240. On exposure to air, these oils dry very slowly to soft, sticky films, and this drying behaviour is not much improved by the addition of well-known driers such as lead, manganese and cobalt resinates, and naphthenates.

Pure normal butenes give about 80% of the theoretical yield of 2-butanol. When the sulphuric acid reaction mixture is diluted with ice or ice-water, 20 to 24% of the butyl alcohol is liberated as such, and this is not increased by repeated extraction of the cold acid solution. The remainder of the alcohol may be liberated by hydrolysing the acid alkyl sulphate by heating.

The treatment of mixtures of olefines containing butenes from cracked gases, with sulphuric acid of less than 1·84 sp. gr., to produce butyl and other alcohols was first described by Ellis and Cohen [23, 1924]. King [30, 1919] used 78% sulphuric acid on pure butenes; and Weizmann and Legg [48, 1922], who were interested in converting *n*-butyl alcohol to secondary butyl alcohol through the butenes, recommended the use of 75% sulphuric acid. Taveau [43, 1932] used 85% sulphuric acid at temperatures below 30° C. (86° F.), and a recent patent to Engs and Moravec [24, 1932, 1933] recommended 90 to 100% sulphuric acid on purified butenes to produce mainly dibutyl sulphate. However, with increasing acid concentrations and high percentages of butenes in the hydrocarbon treated, temperature control becomes increasingly difficult; in the liquid phase the normal butenes are very rapidly sulphonated with little or no polymerization by treating with 70 to 75% sulphuric acid at 20 to 30° C. (68 to 86° F.). When diluted with large proportions of saturated hydrocarbons, higher acid concentrations are advantageous.

The composition of the amylene fraction obtained by vapour-phase cracking has been noted. The pentenes in the five-carbon atom fraction, made by pressure cracking, equal about 30%. Pure normal pentenes give nearly theoretical yields of secondary amyl alcohols, when treated with sulphuric acid of 82 to 90% strength at 15 to 20° C. (59 to 68° F.). Similarly, trimethyl-ethylene and *asym*-methylethylethylene with more dilute acid give nearly quantitative yields of *tert*-amyl alcohol. The only pentene which tends mainly to polymerize under these conditions is *iso*-propylethylene. The latter pentene yields not the secondary alcohol which might be expected, but *tert*-amyl alcohol [51,1933]:



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CHCH{:}CH_2-\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C(OH)CH_2CH_2.$$

The sulphate of this alcohol, in acid of the concentrations required to react with an olefine of this type, rapidly polymerizes. The relatively large proportions of the oils which are formed from cracked petroleum pentene fractions suggests that, as in the case of butadiene, the polymerization of a given olefine includes other olefines not by themselves polymerized under these conditions.

Commercial secondary amyl alcohol consists mainly of 2-pentanol, with about 20% of 3-pentanol. 1-Pentene yields exclusively 2-pentanol; 2-pentene yields a mixture of alcohols containing about 65% 2-pentanol and 35% 3-pentanol.

Secondary diamyl sulphate is readily made in yields of 70 to 75% by treating 90% sulphuric acid slowly, with cooling, with an excess of 2-pentene, maintaining the temperature at 15 to 20° C. Dilution by water precipitates diamyl sulphate and dissolved pentene [8, 1934].

Synthetic methyl, ethyl, and *iso*-propyl alcohols are used in the United States to safeguard automobile radiators against freezing. This is the largest industrial use of these alcohols. *Iso*-propyl alcohol is important as a raw material for the manufacture of acetone, by catalytic dehydrogenation, and for the manufacture of acetic anhydride, through the intermediate conversion of acetone to ketene. The ketones, particularly methyl ethyl ketone, have a growing market as constituents of cellulose ester lacquers. *Iso*-propyl ether has found a limited industrial application in extracting acetic acid from dilute aqueous solutions, and has been found to be valuable, when blended with gasoline, as motor fuel of high anti-knock value.

The conversion of ethane, propane, and butane to gasoline by cracking and polymerization is of growing importance and such installations make potentially available still larger quantities of ethylene and propylene. The value of gasoline will largely determine the basic raw material value of these simple olefines.

REFERENCES

1. Alco Products Co. Cf. Brooks, B. T. *Ind. Eng. Chem.* **27,** 281 (1935).
2. Baldeschwieler, E. L., and Cassar, H. A. *J.A.C.S.* **51,** 2969 (1929).
3. Berl, E., and Schmidt, O. *Angew. Chem.* **36,** 247 (1923).
4. Brooks, B. T. *Chem. Rev.* **2,** 369 (1926).
5. —— U.S.P. 1,879,599 (1932).
6. —— U.S.P. 1,885,585 (1932); 1,919,618 (1933).
7. —— U.S.P. 1,894,661 (1933).
8. —— *J.A.C.S.* **56,** 1998 (1934).
9. —— *Ind. Eng. Chem.* **27,** 287 (1935).
10. Brooks, B. T., and Humphrey, I. W. *J.A.C.S.* **52,** 721 (1930).
11. Bury, E., and Ollander, O. *Gas J.* **148,** 718 (1919).
12. Butlerow, A. *Ann.* **144,** 1 (1867); **180,** 245 (1875); cf. Konowalow, D., *Ber.* **13,** 2395 (1880).
13. Cie Bethune. B.P. 221,512 (1925).
14. Curme, G. U.S.P. 1,422,183 (1922).
15. Curme, H. R. U.S.P. 1,339,947 (1920).
16. Davis, H. S., and Schuler, R. *J.A.C.S.* **52,** 721 (1930).
17. Distillers Co., Ltd. B.P. 368,051 (1932); 370,136 (1934).
18. Drushel, W. A., and Linhart, G. A. *Amer. J. Sci.* **32,** 51 (1911).
19. Ellis, C. *The Chemistry of the Petroleum Derivatives* (Chem. Catalog Co., New York, 1934).
20. —— *The Chemistry of the Petroleum Derivatives,* 161 (Chem. Catalog Co., New York, 1934).
21. —— *Chem. and Met. Eng.* **23,** 1230 (1920).
22. —— U.S.P. 1,464,153 (1923).
23. Ellis, C., and Cohen, M. J. U.S.P. 1,486,646 (1924).
24. Engs, W., and Moravec, R. Z. U.S.P. 1,854,581 (1932); 1,912,695 (1933).
25. Frey, F. E., *et al.* U.S.P. 1,847,238 (1932).
26. Fritzsche, P. *Chem. Ind.* **20,** 266 (1897); **21,** 33 (1898).
27. Geniesse, J. C., and Reuter, R. *Ind. Eng. Chem.* **24,** 219 (1932).
28. Isham, R. M., and Born, S. U.S.P. 1,744,164 (1930); 1,744,207 (1930); Isham, R. M. U.S.P. 1,729,782 (1929); 1,744,227 (1930).
29. Joshua, W. P., and Stanley, H. M. U.S.P. 2,005,500 (1935).
30. King, A. T. *J.C.S.* **115,** 1404 (1919).
31. Lebo, R. M. U.S.P. 1,865,024 (1932).
32. Maimeri, C. B.P. 215,000 (1924).
33. Mann, M. D., and Williams, R. R. U.S.P. 1,365,043 (1921).
34. Merley, S. R., and Spring, O. U.S.P. 1,859,241 (1933); Basore, C. A. 1,385,515 (1922).
35. Nametkin, S., and Abakumovskaja, L. *Ber.* **66** B, 358 (1933).
36. Ormandy, W. R., and Craven, E. C. *J.S.C.I.* **47,** 317 T (1928).
37. Plant, S. G. P., and Sidgwick, N. *J.S.C.I.* **40,** 14 T (1921).
38. Rice, F. O. *Mechanism of Homogeneous Organic Reactions,* 117 (Chem. Catalog Co., New York, 1928).
39. Rochlingsche Eisen u. Stahlw. B.P. 238,900 (1925).
40. Soc. Anon. Explosifs. B.P. 251,652 (1925).
41. Soddy, F. *Chim. et Ind.* **13,** 718 (1925).
42. Strahler, J., and Hachtel, B. *Brenn.-Chem.* **15,** 166 (1934).
43. Taveau, R. M. U.S.P. 1,845,007 (1932).
44. Thomas, C. A., and Carmody, W. H. *Ind. Eng. Chem.* **24,** 1125 (1932).
45. Valette, F. *Chim. et Ind.* **13,** 718 (1925).
46. Voorhees, V., and Youtz, M. A. U.S.P. 1,875,311 (1932).
47. Wagner, C. R. *Refiner,* **8** (11), 80 (1929).
48. Weizmann, C., and Legg, P. A. U.S.P. 1,408,320 (1922).
49. Whitaker, M. J., and Alexander, C. M. *Ind Eng. Chem.* **7,** 484 (1915).
50. Whitaker, M. J., and Rittman, W. *Ind. Eng. Chem.* **6,** 479 (1914).
51. Whitmore, F. C. *Ind. Eng. Chem.* **24,** 1125 (1933).

THE SYNTHESIS OF METHANOL AND HIGHER ALCOHOLS FROM WATER GAS

By D. A. HOWES, Ph.D., A.M.Inst.P.T.
Anglo-Iranian Oil Company Ltd.

1. Introduction

ALTHOUGH the synthesis of methanol and higher alcohols from carbon monoxide and hydrogen is now carried out in many parts of the world on an industrial scale, the process is relatively new. Until 1923 the sole commercial source of methanol (methyl alcohol) was crude 'wood spirit' produced by the destructive distillation of wood—hence one of its names is 'wood alcohol'. In that year consternation was caused in the wood distillation industry by the announcement that a commercially practicable and cheap synthesis of methanol was in actual operation in Germany. This process was then said to produce a high grade of methanol that could be sold at 20–30 cents per gallon. This product was imported into the United States of America (one of the greatest producers of wood spirit) and sold at a price (45 cents per gallon) with which the wood distillers could not compete. The growth of the synthetic methanol industry has been so rapid that the only important remaining outlet for the methanol produced by wood distillation is as a denaturant for ethyl alcohol. The ascendancy of the synthetic industry has also been brought about by the fact that acetic acid, another important product of wood distillation, is now produced more cheaply by synthetic processes employing acetylene as raw material, with the result that wood distillation is now, to a considerable extent, no longer economic.

Synthetic methanol now finds a ready market as a raw material for the production of formaldehyde, as a solvent for lacquers, &c., and as a methylating agent. Considerable quantities are also finding use as a motor-fuel constituent—particularly in fuels intended for use in high-duty engines of the racing type.

2. Historical Development

The first evidences that oxygenated compounds had been formed from water gas in the presence of catalysts and under high pressure are to be found in the patents of the Badische Anilin u. Soda Fabrik which began to appear in 1913 [18, 1913–16]. A product comprising a mixture of aliphatic hydrocarbons, alcohols, and other oxygen-containing organic compounds was claimed. The catalysts consisted of metallic oxides, or mixtures of oxides of such metals as zinc and cobalt promoted with an alkali metal carbonate or hydroxide. One important effect of these patents was to stimulate research on the pressure synthesis of organic compounds from water gas. As a consequence much confusion and controversy arose in regard to the efficacy of the different catalysts, due largely to the use of a diversity of experimental conditions by the many investigators who worked on the subject.

Prior to 1913 the only reactions established by the passage of carbon monoxide and hydrogen over a suitable catalyst were those resulting in the formation of methane, carbon dioxide, and water. Thus, if water gas is passed over a nickel catalyst at atmospheric pressure and at a temperature of 380° C., the product is a mixture of carbon dioxide, methane, and hydrogen. In the presence of excess hydrogen carbon monoxide is almost completely converted to methane at 230–50° C., thus:

$$CO+3H_2 = CH_4+H_2O.$$

At higher temperatures carbon monoxide can decompose and give carbon dioxide plus carbon.

$$2CO = C+CO_2$$

Comprehensive reviews of the work carried out on these reactions have been published by Ellis [9, 1930] and by Marek and Hahn [27, 1932].

After the publication of the above-mentioned patents intensive work was carried out by Fischer in Germany and by Patart in France. Fischer attacked the problem mainly from the point of producing a mixed product suitable as fuel for internal-combustion engines. He employed as catalyst iron impregnated with a strong base and the conditions were 410° C. and 70–150 atm. pressure. The product consisted of a mixture of aldehydes, ketones, and organic acids together with a series of hydrocarbons up to C_9 and boiling from 60 to 200° C. The Badische Company and Patart endeavoured to determine the conditions under which single pure compounds, e.g. methanol, could be produced. Patart, using a zinc oxide catalyst at 400–25° C. and 150–250 atm. pressure, obtained a liquid product containing 80% methanol, some water, and higher alcohols. Methane and carbon dioxide were also formed to some extent. The Badische Company developed catalysts consisting of mixed zinc and chromium oxides and obtained good yields of methanol under conditions similar to those used by Patart. Audibert also obtained pure methanol at 225–300° C. and 200 atm. pressure by using catalysts comprising the oxides of chromium and uranium. Audibert demonstrated that only above 300° C. did side reactions begin which resulted in the formation of higher alcohols and methane.

The early work of Patart is fully described in *Chemie et Industrie* for November 1926. The plant which he developed was a semi-commercial one, producing 150–200 kg. per 24 hours. Very many catalysts were examined and the best were found to consist of mixtures of zinc oxide and chromic oxide. These gave satisfactory yields and proved least susceptible to loss of activity. Using a pressure of 150–250 atm. methanol was produced at 350–400° C. and higher alcohols at 400–50° C. Patart stated that any gas could be used for treatment provided the carbon monoxide+hydrogen content is greater than 30% and the carbon monoxide content at least half the hydrogen content. The reaction then proceeds at a rate proportional to the partial pressure of the reactants.

During the period 1926–33 a very large number of patents were granted covering various phases of synthetic methanol production from water gas, in particular applying to the catalysts used. This period saw the development of the synthetic methanol industry in Germany by the I. G. Farbenindustrie, in England by Synthetic Ammonia & Nitrates Ltd. (now a constituent company of Imperial Chemical Industries), and in America by the Dupont Ammonia Corporation and others. Also plants are now in operation in Italy, Japan, and Russia. In addition to the production of methanol, higher alcohols, particularly propanols, butanols, and pentanols, are also synthesized by this reaction, and in America find a market as solvents and denaturants. The development of processes by which liquid hydrocarbons are produced from water gas has been much less rapid, and the first commercial plants are only now in course of erection.

3. The Methanol Synthesis Reaction

The reaction involved in the production of methanol from carbon monoxide and hydrogen is

$$CO+2H_2 \rightarrow CH_3OH.$$

This reaction is reversible and is therefore governed by the laws of reaction equilibria. Because it involves a reduction in volume (3 volumes reactants give 1 volume of product) it is favourably influenced by the use of super-atmospheric pressure, and because the synthesis reaction is exothermic, it follows that it should be best carried out at low temperatures. Furthermore, a suitable catalyst is necessary in order to promote the reaction at temperatures low enough to prevent the formation of methane, which proceeds according to the equation

$$CO+3H_2 \rightarrow CH_4+H_2O$$

and is also favourably affected by increased pressures. Catalysts chosen for the methanol synthesis reaction must exclude nickel and cobalt because these substances also catalyse methane formation.

(*a*) **Equilibrium Data.**

Although the methanol equilibrium has been the subject of intensive investigation, striking discrepancies still exist in the values which have been obtained. Kelley [23, 1926] made an attempt to calculate the equilibrium from physical data and arrived at the following equation for the free energy change of the reaction

$$\Delta F = -21{,}300+32{\cdot}2T\log T-0{\cdot}00825T^2-42{\cdot}5T.$$

The equilibrium constant is then given by

$$\log_n K_p = \Delta F/(-RT).$$

These results have been criticized. Audibert and Raineau [2, 1927–8] produced the following equations for the methanol equilibrium, starting with a gaseous mixture of the composition $CO+2H_2$. The fraction x of carbon monoxide converted into methanol is approximately given by Nernst's method of evaluation

$$\frac{\log(1-x)^3}{x(3-2x)^2} = \frac{-27{,}000}{4{\cdot}571T}+3{\cdot}5\log T+2{\cdot}99794+2\log P.$$

This relationship may be expressed on the basis of partial pressures and equilibrium constant as follows:

$$\log K_p = \frac{P(\text{MeOH})}{P_{CO}(P_{H_2})^2} = \frac{27{,}000}{4{\cdot}571T}-3{\cdot}5\log T-3{\cdot}6.$$

From this expression it appears that Audibert and Raineau, by taking the algebraic sum of the chemical constants as 3·6, deduced an equation for the equilibrium constant in close agreement with experimental results [33, 1928]. Kelley derived the free energy of the reaction at 298° Abs. from data which do not involve the specific heat of methanol in the gaseous phase, and it is probable that incorrect assumptions have been made for this temperature effect in the calculations of the free energy change at higher temperatures. Results obtained at the Chemical Research Laboratory, Teddington, England, have been found in good agreement with Audibert's formula [33, 1928]. Lewis and Frolich [26, 1928] have stated that 'calculations of the methanol equilibrium are bound to be more or less inaccurate owing to the lack of adequate data on the specific heat and the equation of state of the alcohol.' Kelley has recalculated his earlier values, using new data, and has, with caution, proposed the equation

$$\Delta F_{298}{}^\circ = -9{,}640 \text{ cal.} \quad \text{and} \quad \Delta H_{298} = -25{,}150 \text{ cal.}$$

$$\Delta F = -20{,}740+4{,}500T\log_{10}T-0{\cdot}01586T^2+IT,$$

where $I = 69{\cdot}4$.

Francis [14, 1928] gives the following expression:

$$\Delta F = -26{,}370+49{\cdot}97T,$$

which gives the following figures:

227° C. $\Delta F = -1{,}420$
327° C. $\Delta F = +3{,}570$
427° C. $\Delta F = +8{,}560$

The discrepancy between calculated and determined values of K_p is ascribed to inaccuracies in the heat of combustion of methanol. The limitations of any such calculations are shown by the fact that even if the heat of combustion of methanol were known to an error of only 0·1%, the value of K_p for the reaction at 298·1° K. would still be in error to the extent of 33% [22, 1930]. The figures quoted by Audibert, Kelley, and Francis are compared in Table I, from which it is evident that those of the two last named are of the same order of magnitude, but between them and those derived from Audibert's equation there is a discrepancy which increases as the temperature rises. Smith and Branting found by experiment that at 303·8° C. the value of K_p was $5{\cdot}57\times10^{-4}$, with a probable error of ±5%. This agrees fairly well with Audibert's calculated value at 300° C.

TABLE I

Methanol Equilibrium Constant

Temperature		*Equilibrium constant* $K = \frac{(CH_2OH)}{(CO)\cdot(H_2)^2}$ *according to*		
Absolute	*° C.*	*Audibert*	*Kelley*	*Francis*
300°	27	$2{\cdot}65\times10^7$	$6{\cdot}7\times10^7$	..
400°	127	$1{\cdot}15\times10^2$	$20{\cdot}6\times10^2$	..
500°	227	$5{\cdot}75\times10^{-2}$	$316{\cdot}0\times10^{-2}$	417×10^{-2}
600°	327	$3{\cdot}20\times10^{-4}$	$386{\cdot}0\times10^{-4}$	500×10^{-4}
700°	427	$7{\cdot}55\times10^{-6}$	$1{,}540{\cdot}0\times10^{-6}$	$2{,}100\times10^{-6}$

Determinations of the methanol equilibrium have also been made by Newitt, Byrne, and Strong [34, 1929], who approached equilibrium from both sides—i.e. synthesis and decomposition, and who used both static and flow methods of experimentation. The conditions employed were 280–338° C. and 60–100 atm. pressure—a catalyst being employed consisting of $3ZnO–Cr_2O_3$ to which 0·5% copper nitrate was added.

The results revealed a linear relationship between free energy and absolute temperature:

$$\Delta F = 70{\cdot}5T-30{,}500.$$

The values of K_p found were as follows and are considerably lower than any corresponding values either calculated or experimentally obtained by previous workers.

Temp. ° C.	K_p	*Temp. ° C.*	K_p
260	$1{\cdot}2\times10^{-3}$	340	$2{\cdot}9\times10^{-5}$
280	$4{\cdot}5\times10^{-4}$	360	$1{\cdot}3\times10^{-5}$
300	$1{\cdot}6\times10^{-4}$	380	$6{\cdot}3\times10^{-6}$
320	$6{\cdot}7\times10^{-5}$		

The correct determination of the methanol equilibrium is of considerable commercial as well as scientific interest, inasmuch as such values are the best criteria of the efficiency of a catalyst at a given temperature. For example, if by using a given catalyst at a certain temperature a quantitative yield of methanol near to that of the equilibrium proportions predicted by the experimental *Kp* values at such temperature were readily secured, the quest for a more active catalyst would be unnecessary.

(*b*) Catalysts for the Synthesis of Methanol from Water Gas.

The technical and patent literature contains references to hundreds of different types of catalyst mixtures which may be used under a wide variety of conditions. Such catalyst masses may be conveniently divided into three classes:

1. Mixtures of metallic oxides.
2. Mixtures of metals or alloys.
3. Mixtures of oxides and metals, or a metal plus an oxide or a salt as promoter.

The work done by the Badische Anilin u. Soda Fabrik (later known as the I. G. Farbenindustrie) is shown by the large number of patents issued dealing with suitable catalysts—the first of which were issued in 1913 and 1914. These describe the preparation of hydrocarbons and oxygenated compounds by passing mixtures of the oxides of carbon along with hydrogen or compounds containing hydrogen over suitable catalysts at high temperatures and at pressures of more than 5 atm. The nature of the products obtained depended upon the type of catalyst and upon the other experimental conditions and varied greatly with variation in these factors. The catalysts which were first mentioned represented a large number of elements and their compounds, such as cerium, chromium, cobalt, manganese, molybdenum, osmium, palladium, titanium, tungsten, and zinc. These elements were to be employed in different states of aggregation, such as powder, filings, wool, gauze, &c., or in the form of their oxides or other compounds. They could also be present as mixtures in various combinations by weight. To these mixtures, basic substances, such as the alkali hydroxides, carbonates, &c., could be added to advantage. Various carriers such as asbestos, pumice, and magnesium oxide were suggested. Poisons, such as sulphur in various states of combination, had to be avoided by purifying the reacting gases. Iron in any part of the surfaces of the apparatus exposed to the reacting gases was also to be avoided. Temperatures which are mentioned in the examples given range from 250 to 420° C. and pressures from 50 to 250 atm. The proportions of $CO:H_2$ by volume vary from 2:3 to 2:1.

It is at once apparent that the specifications mentioned in these patents are very broad in their scope and seem designed to cover the use as catalysts of practically all combinations of the elements and their compounds, with the single exception of iron. In succeeding patents [10, 1924–5] specific combinations of different catalysts, together with details regarding the methods employed in their preparation, have been given for the synthesis of methanol relatively free from other products in distinction to the early patents which claimed mixtures. The notable changes which were made in the process in order to obtain pure methanol are to be found chiefly in the nature of the catalysts used. Instead of the metallic oxide catalyst which was promoted by the addition of small amounts of an alkali, catalysts of the same general type but without the alkali were proposed. In general mixtures of two or more metallic oxides with the more basic one in excess have been used.

Because Sabatier had previously found zinc oxide alone to be a good catalyst for the decomposition of methanol, Patart [36, 1924–5] examined this substance as a synthetic catalyst. It proved to be only very slightly active and Patart turned to catalysts consisting of mixed oxides. The best catalyst examined comprised a mixture of zinc oxide and copper (or copper oxide) with the admixture of compounds of chromium. The success of the operation was found by Patart to be dependent upon the following factors:

(*a*) The complete elimination of all metals except tin, aluminium, and copper from those parts of the plant which come in contact with the carbon monoxide in the reacting gas. Iron, nickel, and cobalt must be avoided because these form carbonyls which decompose on the catalyst and destroy its activity.

(*b*) The catalysts must not contain alkali—otherwise they yield a product containing hydrocarbons and higher alcohols.

Audibert and Raineau [2, 1927–8] found that zinc oxide gave a 17·5% conversion to methanol at 150 atm. and an inlet gas rate of 5,000 volumes (at N.T.P.) per volume of catalyst per hour, but that, in common with other single component catalysts, it was very sensitive to temperature and suffered rapid loss of activity on overheating. Manganous oxide under the same conditions gave a 5% conversion, but less than 2% conversion was obtained with zirconium oxide, cerous oxide, uranium oxide (UO_2), or beryllium oxide. Alumina, silica, blue molybdenum oxide, vanadium trioxide, blue tungsten oxide, thoria, titania, magnesia, lime, barium oxide, and strontium oxide were all found to be inert. Catalysts such as metallic iron, nickel, or cobalt are also worthless for methanol synthesis because, although they are often active in reducing carbon monoxide to methanol, they have a more pronounced effect on the following side reactions leading to the production of methane, carbon, carbon dioxide, and water:

$$2CO = C + CO_2$$
$$CO + 3H_2 = CH_4 + H_2O$$
$$2CO + 2H_2 = CH_4 + CO_2.$$

The most satisfactory methanol catalysts, and also those which are apparently now used commercially, consist of zinc oxide-chromium oxide. Other effective catalysts are zinc oxide-copper oxide and zinc oxide-copper oxide-chromium oxide in various ratios.

Zinc Oxide Catalyst. Brown and Galloway [6, 1928] have made an elaborate study of the behaviour of zinc oxide as a methanol synthesis catalyst, and have concluded (cf. Patart above) that it is much less active than other catalysts, such as normal and basic zinc chromates, and also short-lived. These investigators prepared their catalyst by precipitating hot solutions of zinc nitrate with sodium carbonate and washing it free from nitrate. The moist precipitate was pressed into threads.

A claim has been made that a zinc oxide catalyst for methanol synthesis may be prepared which is highly active without a promoter, such as chromium oxide, and which is not usefully improved by the addition of a promoter. According to this procedure zinc carbonate is precipitated from a very dilute solution in the presence of protective colloids such as starch, saponin, pectin, or hydrated silica. Electrolytes are removed by thorough washing and the zinc carbonate gel is dried by heating under reduced pressure. The conversion to oxide by heating is carried out at 250–400° C. [5, 1927].

Zinc Oxide-Copper Oxide Catalysts. Of particular interest with regard to catalysts comprising the mixed oxides of zinc and copper is the work of Frolich, Fenske, and Quiggle [15, 1928], who found that the most efficacious catalyst for methanol decomposition was one prepared by co-precipitation of the corresponding hydroxides, as shown by the figures reproduced in Table II. Using such a method of preparation the effect of variations in the proportions of the two constituents was examined. The results obtained (all of which were on methanol decomposition and not on methanol synthesis) may be summarized as follows:

1. The maximum decomposition of methanol and formation of carbon monoxide occurs when the zinc oxide is present in excess.
2. Between 40 and 50 mol. % zinc oxide, the mols. of carbon monoxide formed per mol. of methanol increase about 350%.
3. The addition of a small amount of zinc oxide to copper oxide markedly increases the decomposition of methanol. A catalyst composed of 3 mol. % zinc oxide and 97 mol. % copper oxide decomposes 26% of the methanol, whereas pure copper oxide decomposes only 9% under otherwise constant conditions.
4. A similar promoter effect is observed when a small amount of copper oxide is added to zinc oxide.
5. Copper promoted with zinc oxide especially favours the formation of methyl formate, while carbon monoxide formation is favoured by zinc oxide promoted with copper.

Lewis and Frolich [26, 1928] have employed a catalyst comprising copper oxide 44%, zinc oxide 36%, and alumina 20% in methanol synthesis. The catalyst mixture was supported on metallic copper in the proportion of 1: 3, the function of the copper being to minimize local overheating due to the exothermic reaction involved.

TABLE II

Comparative Efficiency of Copper Oxide-Zinc Oxide Catalyst prepared by various methods [15, 1928]

Composition of Catalyst 95 mol. % copper oxide, 5 mol. % zinc oxide

Method of preparation	*Methanol decomposition efficiency*
Zinc hydroxide precipitated on suspended copper hydroxide	75
Copper hydroxide precipitated on suspended zinc hydroxide	67
Hydroxide gels mixed	83
Calcined nitrates	70
Co-precipitation of hydroxides . . .	100

Zinc Oxide-Chromium Oxide Catalysts. During the active period of the development of the synthetic methanol process zinc oxide and chromium oxide were known to be important constituents of active catalysts and were mentioned in the basic patents of 1913 [18, 1913–16]. A considerable number of more recent patents have specified zinc oxide alone or mixtures of these two oxides in various proportions, and it may be stated that such mixtures constitute the most satisfactory catalysts yet developed for methanol synthesis. In 1926 G. Patart reported [37, 1926] that the best methanol catalysts known to him consisted of mixtures of zinc and chromium oxides because these gave satisfactory practical yields, are easy to prepare, persistent in activity, have great insensitiveness to poisons, and are easily regenerated. More recently Bone has stated that the best methanol catalyst seems to be $3ZnO.1Cr_2O_3$ to which has been added a fractional percentage of copper nitrate [4, 1930].

The presence of chromium prevents in marked degree the loss of activity suffered by catalysts of high zinc content when exposed to temperatures somewhat above the optimum operating temperature. Catalysts in which the mol. ratio Cr:Zn = 1·0 have, in fact, shown continuous improvement during an extended period of use at a temperature above that giving maximum activity [30, 1935], although Audibert [3, 1931] has said that the exposure of catalysts to temperatures higher than the normal operating temperature should at all times be avoided. Lazier has claimed [25, 1930], however, that catalysts prepared by ignition at 650–1,000° C. are unaffected by use at high temperatures.

With regard to catalyst composition, the most active chromium-zinc methanol catalysts are those containing excess of zinc. The agreement on this point in the literature is very good. Frolich [16, 1928] has stated, 'probably the most interesting fact . . . is the necessity of having the more basic oxide in excess'. This point is repeatedly emphasized in the patent literature, and is also brought out clearly by the work of Cryder and Frolich [8, 1929]. These workers found that at 350° C. and 204 atm. pressure the maximum production of methanol occurred with a catalyst containing 77 mol. % zinc and 23 mol. % chromium, in which case 18% of the carbon monoxide was converted. Similarly, in methanol decomposition experiments carried out at 340° C. and 1 atm. pressure, a maximum yield of carbon monoxide, equivalent to 85% of the methanol converted, was obtained with a chromium-zinc catalyst containing 75 mol. % zinc. Catalysts richer in chromium gave relatively large yields of carbon dioxide and unsaturated hydrocarbons, while those richer in zinc tended to produce methyl formate. The activity of the catalysts, as indicated by the total quantity of methanol decomposed under the conditions employed, was a maximum at a catalyst composition of 78 mol. % zinc.

Important experimental work on chromium-zinc catalysts in methanol manufacture from water gas has been published by Morgan, Taylor, and Hedley [33, 1928]. The method of testing was to place a quantity of catalyst in a heated static reaction vessel, fill the latter with hydrogen-carbon monoxide mixture at 200 atm. pressure, and measure the time taken for a certain small pressure decrease. As a result of these tests Morgan and his co-workers concluded that a catalyst prepared from either basic or normal zinc chromate would probably be efficient for methanol synthesis and also that the optimum temperature should lie between 350 and 400° C. It was further found that, with a catalyst prepared from either normal zinc chromate or the basic salt, $3ZnO–CrO_3$, working at 420° C. and 200 atm. pressure and a space velocity of 33,300 volumes of inlet gas per volume of catalyst per hour, the hourly make of liquid organic products was about twice the catalyst volume. The liquid was homogeneous and contained 95% methanol, 1% of higher alcohols, and 4% of water. The addition of alkaline substances to the zinc chromate catalyst favoured the formation of higher alcohols. When varying quantities of cobalt chromate were added to the catalyst, methanol remained the main constituent of the product, but higher alcohols, including ethyl alcohol, were produced in appreciable quantities, together with small amounts of aldehydes. When mixed catalysts were employed containing, in addition to chromium and zinc, also cobalt, copper, and manganese, alcohols in addition to methyl and ethyl alcohols were identified in the products, namely, *n*-propyl, *n*-butyl, and *iso*-butyl alcohols.

Important investigations of a similar character have also been made by Huffman and Dodge [21, 1929], who carried out methanol decomposition experiments at 350° C. with catalysts varying in composition from pure zinc oxide to pure chromic oxide and prepared by precipitation of the hydroxides from solutions of the mixed nitrates by addition of ammonia solution. After washing and drying at 110° C. the catalysts were reduced by hydrogen at temperatures up to 300° C. before being used. It was found that the addition of a small amount of chromium oxide to zinc oxide caused a decrease in the total decomposition of methyl alcohol, contrary to the effect noticed in synthesis experiments. If, however, only the decomposition into carbon monoxide plus hydrogen is considered, the effect is in accord with that observed in synthesis experiments. In all the decomposition tests catalyst deterioration was marked, probably due to the deposition of the heavier decomposition products—unsaturated compounds, &c.—on the catalyst. The results obtained by Huffman and Dodge differ in some respects from those of Frolich and his co-workers, but the catalyst having the maximum decomposition activity was found to have the composition Zn/Cr = 4·0, in close agreement with Frolich's work.

The most extensive investigation on zinc-chromium catalysts in methanol synthesis is that of Molstad and Dodge [30, 1935], who have examined a very wide series of these catalysts over a wide temperature range at a pressure of about 180 atm. It was found that the catalyst containing 25 atomic % chromium and 75 atomic % zinc, both metals being initially in the form of oxides, was the most active of the series. This observation is in good agreement with the above-mentioned results of other investigators. Continued testing, however, disclosed that some catalysts were affected very differently by high-temperature operation. Catalysts containing less than 25 atomic % chromium suffered a decrease in activity during use at high temperatures, while those containing more than this quantity of chromium improved. This effect, which is not revealed in tests of short duration, indicated that the most active catalyst of this type was one containing about 50 atomic % chromium. This catalyst produces very nearly pure methanol, appears to be uninjured by long use or by operation at temperatures considerably above the normal operating temperatures, and has good physical ruggedness. It is preferably made by precipitation from a solution of the mixed nitrates by ammonia. Catalysts prepared by several methods which used chromic acid as the source of chromium were much less active than those in which the chromium was initially in the trivalent form. Molstad and Dodge also found by both synthesis and decomposition tests that addition of up to 25 mol. % zinc oxide to chromium oxide gives a catalyst of lower activity than chromium oxide alone. Precipitation of zinc oxide by sodium carbonate was found to give a more active catalyst than when ammonia was used as the precipitating agent. The most active zinc oxide catalyst was made by using a slight insufficiency of sodium carbonate.

Zinc-chromium catalysts in the initial form of chromates have also been examined by Brown and Galloway [6, 1928] whose results are reproduced in Table III. These workers have also shown [7, 1929–30] that di-methyl-ether is an important by-product in methanol synthesis when normal zinc chromate catalyst is used, but the amount formed is small, ranging from 0·7 to 5·2% conversion of carbon monoxide per pass.

TABLE III

Results of Brown and Galloway

Catalyst: Reduced basic zinc chromate. Pressure 180 atm.; Temperature, 400° C.

Catalyst Conditions of reduction	*Vol. ml.*	*Wt. g.*	*Zinc oxide content g.*	*Methanol yield g. per hour*	
				Space velocity	
				16,000	*7,500*
1. At 40 atm. of 1:2 mixture of CO:H_2. Slowly raised from 25 to 370° C. . .	250	165	112·5	129·3	..
2. Hydrogen at 1 atm. Reduction began at 300° C., but temperature uncontrolled and allowed to rise to 450° C.	250	153	104·0	89·2	60·8
3. Reduced at 275–325° C. at 1 atm. with a mixture of 5% hydrogen and 95% carbon monoxide . .	250	170	115·5	106·4	94·5

Numerous important references to zinc-chromium methanol catalysts are made in the patent literature.

A proposal has been made to prepare such catalysts by heating a mixture of zinc carbonate or basic zinc carbonate and a chromium compound such as zinc chromate or basic zinc chromate. With zinc chromates the heating must be effected in the presence of reducing gases [39, 1926]. Smith [38, 1926] has suggested the preparation of catalysts from a basic zinc chromate of the composition $4ZnO \cdot CrO_3$, while the following methods of preparation have been put forward [40, 1926]:

(*a*) Precipitation with soda-ash solution of a mixture of sodium bichromate or chromate with sulphuric acid to which zinc has been added.
(*b*) Precipitation with soda-ash solution of the spent electrolyte of a bichromate electrolyte cell.
(*c*) Precipitation with soda-ash solution of commercial basic chrome liquor with added zinc sulphate.

The proportions of zinc and chromium are preferably so chosen that the precipitate contains 70–80 atomic proportions of zinc to 30–20 atomic proportions of chromium. To regenerate these catalysts after use they are dissolved in sulphuric acid and precipitated with sodium carbonate [41, 1928].

4. The Production of Higher Alcohols from Water Gas

The catalysts employed for the synthesis of substantially pure methanol from water gas may be modified to give products containing valuable quantities of higher alcohols.

Usually zinc-chromium catalysts containing alkaline substances—e.g. free alkalis—are employed for this purpose.

Morgan, Taylor, and Hedley [33, 1928] have described the preparation of such catalysts, of which the following is an example: zinc oxide, 15 parts by weight; potassium chromate, 23·5 parts; potassium carbonate, 11·5 parts. The catalyst was prepared in the form of granules and tested in a static plant at 370° C. The fall in pressure from an initial pressure of 200 atm. was 60 atm. in 75 sec. and 90 atm. in 6 min. In a circulatory apparatus and at low gas velocities the product separated into two layers, and the lower the gas velocity the greater was the proportion of the upper layer of partially miscible alcohols and esters. An examination of the composition of this product showed it to contain methanol and higher alcohols mixed with esters and free acids. Morgan, Hardy, and Proctor have dealt with alkalized catalysts in greater detail in a more recent publication [32, 1932]. A basic catalyst, containing a mixture of chromium and manganese oxides in molecular proportions, was impregnated with various amounts of the hydroxides of the five alkali metals, and these alkalized catalysts were tested in the methanol synthesis reaction. The results of these tests are reproduced in Table IV.

TABLE IV

Impregnating alkali expressed as combined metal	*% by weight impregnating material*	*% gas converted per passage*	*Yield of product, g. per hr.*	*Density of product*	*Carbon content of crude product, %*	*Methanol in product, %*	*Carbon present as compounds other than methanol, %*	*Conversion of carbon into compounds other than methanol, g. per hr.*	*Volume of material insoluble in $CaCl_2$ solution (c.c. per 100 g.)*	*Yield of material insoluble in $CaCl_2$ solution (c.c. per hour)*
None	..	3·5	62	0·8235	34·7	80·5	13·0	2·8	0·3	0·2
Lithium	3·4	2·7	47	0·8265	36·8	76·9	21·7	3·8	3·55	1·7
	6·7	2·6	45	0·843	34·7	73·7	20·3	3·2	6·26	2·8
	10·1	2·3	40	0·834	35·8	71·7	24·9	3·6	4·42	1·8
Sodium	2·8	2·4	43	0·855	35·7	63·9	32·9	5·0	12·8	5·5
	6·3	1·2	21	0·883	33·2	55·0	37·9	2·6	14·4	3·0
	9·8	1·0	17	0·893	31·0	50·1	39·4	2·1	14·05	2·4
Potassium	1·5	2·7	47	0·8175	36·7	81·8	16·4	2·8	0·63	0·3
	3·9	2·2	39	0·8505	37·0	60·8	38·4	5·5	12·8	5·0
	4·9	1·9	33	0·8775	37·0	50·7	48·6	5·9	21·5	7·1
	5·7	1·6	29	0·8815	34·8	53·0	42·9	4·3	18·6	5·4
	8·4	1·4	24	0·8985	34·6	52·2	43·4	3·6	17·5	4·2
	11·9	1·5	27	0·9085	34·2	49·0	46·3	4·3	23·0	6·2
Rubidium	2·3	3·4	61	0·8325	36·8	75·5	23·1	5·2	4·62	2·8
	4·4	3·5	62	0·847	37·7	67·2	33·1	7·7	17·8	8·8
	9·8	3·0	53	0·881	34·5	49·7	46·0	8·4	28·7	15·2
Caesium	1·8	3·5	62	0·825	35·3	79·5	16·2	3·6	1·53	1·0
	3·8	3·0	53	0·818	37·9	82·1	18·8	3·8	1·58	0·8
	8·9	3·3	58	0·849	38·2	63·7	37·5	8·3	16·4	9·5

The percentages of carbon present as compounds other than methanol and the volumes of material insoluble in calcium-chloride solution show that the percentage of higher alcohols in the liquid product increases as the alkali content of the catalyst is raised. Impregnation with lithium, sodium, or potassium hydroxide diminished the yield of liquid product in amount proportional to the concentration of alkali in the catalyst, while rubidium or caesium hydroxide had little effect upon the output. From this it followed that catalysts containing rubidium or caesium gave the highest conversion to higher alcohols, and, as will be seen in Table IV, the catalyst containing 9·8% of rubidium gave the greatest yield of these compounds. These observations are in agreement with those of Fischer and Tropsch [11, 1924], who found that rubidium hydroxide was the most efficient alkali for impregnating the iron chips which they used as catalyst for the production of 'synthol'. These rubidia- and caesia-impregnated catalysts exhibited fairly long periods of initial activity during which the yield of product was as much as 20% higher than normal, but the initial high yields gradually decreased and, after a few hours, reached a steady value. A chromium-manganese catalyst containing 15% of rubidium was also used without giving any appreciable decrease in yield of liquid product, of which a large quantity was prepared and examined in detail. The products identified included methanol, a trace of ethyl alcohol, propanol and isobutanol, 2-methyl butanol, 2-methyl pentanol, and 2-3-dimethyl pentanol. Aldehydes were also detected, including formaldehyde, propaldehyde, hydroxyaldehydes, and unsaturated aldehydes.

Higher alcohol-producing catalysts work at slightly higher temperatures (about 400° C.) than those producing mainly methanol.

Morgan, Taylor, and Hedley [33, 1928] have also used cobalt-containing catalysts for higher alcohol production, since the successful use of this element by Fischer and Tropsch [13, 1926], in the production of hydrocarbons from carbon-monoxide and hydrogen, suggested that it had the special property of linking carbon atoms together. A catalyst prepared from cobalt nitrate and basic zinc chromate effected the production of a whole series of higher alcohols, although methanol remained the major portion of the product. Some results on cobalt catalysts are as follows:

Catalyst	*Temp. ° C.*	*Products*		
		Methanol %	*Higher alcohols %*	*Water %*
Basic zinc chromate + 10% cobalt chromate . .	400	82	9·0	8·0
Basic zinc chromate + 10% cobalt chromate . .	450	90	1·6	8·4
Basic zinc chromate + 5% cobalt chromate . .	400	88·5	5·0	6·5

Fractional distillation of the higher alcohols produced with the first catalyst showed that four-fifths of this portion of the product consisted of *n*-propanol and isobutanol, the latter slightly predominating. The remaining fifth consisted of a mixture of alcohols boiling mainly at 115–16° C. Experiments with a catalyst made from a mixture of 2 parts cobalt nitrate, 1 part zinc manganate, and 0·7 part copper carbonate gave a product of the following composition (on a water-free basis): aldehydes 1·4, methanol 79·7, ethanol 11·6, higher alcohols 7·3. The amount of water formed was 40% of the crude product.

Using a catalyst made from a mixture composed of zinc oxide 10 parts, chromic acid 20 parts, cobalt nitrate 60 parts, and copper carbonate 10 parts, a product was obtained containing 45% of water. Alcohols were present in the product in the following proportions: methanol 77, ethanol 20·3, higher alcohols 2·7.

The Production of Ethyl Alcohol from Water Gas. The production of ethyl alcohol by the catalytic treatment of water gas has been a matter of some controversy, but recent work by Morgan and his co-workers at the Chemical Research Laboratory, Teddington, England, and by others, has demonstrated that this very valuable material may be produced in quantity by this method. Taylor [42, 1934] has shown that, at 175–200 atm. pressure and 380–435° C., in the presence of a catalyst comprising 0·05 mols. cobalt oxide added to 1 mol. of copper oxide and 1 mol. of manganese oxide, 12% of the carbon monoxide reacting is converted into ethyl alcohol, and at the same time 47% is hydrogenated to methane. Catalysts containing cobalt sulphide were found to give the highest conversions to ethyl alcohol, the optimum catalyst composition being a 10:10:1 molecular mixture of copper oxide, manganese oxide, and cobalt sulphide. At 400° C. and 200 atm. pressure this catalyst gave a product, the carbon distribution in which was: methanol 17%, ethyl alcohol 22%, higher alcohols 11%, and methane 47%.

Klyukvin, Volnov, and Karpinskii [24, 1934] have employed zinc oxide-cobalt oxide catalysts of 3:1 mol. ratio composition at 120 atm. pressure and 320–30° C., and have claimed a 39% yield of ethyl alcohol, in addition to higher alcohols, under these conditions.

(*a*) Nature of the Higher Alcohols Produced.

The nature of the higher alcohols produced by this process, as well as their quantity, is, of course, a function of both the catalyst employed and the operating conditions. Mittasch [28, 1926] states that the following alcohols are produced: methanol, ethanol, *n*-propanol, isobutanol, 'amyl' alcohol b.p. 128°, hexanol b.p. 148°, heptanol b.p. 160–5°, and octanol b.p. 180° C. He also states that the predominant higher alcohols appear to be of the type $CHRR'{-}CH_2OH$.

The product from a 15% rubidium catalyst, operating at 400° C. and at 200 atm., with a space velocity of 53,000 reciprocal hours and an inlet gas composition of 2 volumes of hydrogen to 1 volume of carbon monoxide, has been fully examined by Morgan, Hardy, and Proctor [32, 1932] with the following results:

The product was distilled and collected in two fractions after being refluxed with magnesium oxide to fix the acid constituents. In this way was obtained

B.p. up to 85° C., 67% by weight.
B.p. above 85° C., 23% „ , containing 45% non-aqueous material.

The distillate boiling up to 85° C. contained methanol, 62%, and ethyl alcohol, 2·1%. The residue boiling above 85° C. was fractionated after the removal of aldehydes, acetates, &c., with the following results:

B.p. 80–103° C.	5·8%
103–12·5° C.	9·0%
112–22·5° C.	1·4%
122·5–127° C.	1·3%
127–31° C.	0·9%
131–3° C.	2·1%
133–6° C.	0·4%
136–42° C.	2·8%
142–5° C.	1·9%
145–50° C.	1·4%
72–88° C./40 mm.	10·2%
88–93° C./40 mm.	8·7%
80–105° C./10 mm.	10·5%
105–14° C./10 mm.	9·5%
114–22° C./10 mm.	3·2%
Residue	30·9%

The following alcohols were identified in the appropriate fractions: isobutanol, *n*-butanol, 2-pentanol, 2-hexanol, and 2-3-dimethyl pentanol.

The properties of the 85–162° C. fraction of the higher alcohols produced at the Belle plant of the Du Pont Ammonia Corporation have been given as follows [19, 1931]:

Boiling range

85–129° C.	3·5% by wt.	162–5° C.	0·3% by wt.
129–32° C.	25·1% „	165–70° C.	1·0% „
132–8° C.	18·7% „	170–5° C.	1·0% „
138–42° C.	11·1% „	175–80° C.	1·4% „
142–7° C.	20·1% „	180–5° C.	0·3% „
147–52° C.	5·9% „	185–91° C.	1·0% „
152–8° C.	3·1% „	191–6° C.	0·3% „
158–62° C.	5·9% „	Residue	0·2% „
			98·9%

The primary alcohols were separated by esterification with phthalic anhydride in benzene solution. The resulting monophthalates were saponified with caustic soda and the liberated primary alcohols removed by steam distillation. Of the crude product 48·5% consisted of primary alcohols, while the unesterified fraction was found to be quite free of acids, esters, ketones, olefines, and other hydrocarbons and also tertiary alcohols, and, therefore, consisted of saturated secondary alcohols. The primary alcohols were separated by fractional distillation in a 4-ft. column, ⅝ in. in diameter, packed with crystalline silicon carbide and operating at a reflux ratio of 10:1, and the substances detailed in Table V were identified.

The secondary alcohols distilled as follows:

Below 120° C.	5·3%	153–60° C.	0·6%
120–34° C.	3·0%	160–1° C.	0·5%
134–9° C.°	35·3%	161–5° C.	0·9%
139–44° C.	3·0%	165–9° C.	1·1%
144–53° C.	0·8%	169–74° C.	0·5%
			51·0%

The 134–9° C. fraction gave, on refractionation, a substance b.p. 137–8° C., which analysis showed to be a heptanol (m.w. 113, 73·3% C, 13·1% H). Its identity was proved by comparison to be 2-4-dimethyl 3-pentanol. Isopropanol was not isolated but identified by oxidation to acetone; it was only present in very small amounts. 2-methyl 2-butanol, 3-methyl 2-butanol, 3-pentanol, 2-pentanol, and 2-methyl 3-pentanol were also identified.

Mechanism of the Formation of Higher Alcohols from Water Gas.

As may be expected, there is some divergence of opinion regarding the course of the reactions which would serve

TABLE V

Primary Alcohols in Higher Alcohols produced by the Du Pont Ammonia Corporation [19, 1931]

	Boiling-point, ° C.		*Neutralization equivalents of 3-nitro-phthalate*		*Melting-point of 3-nitro-phthalate, ° C.*			
Substance	*Found*	*Literature*	*Found*	*Calculated*	*of substance*	*of known material*	*Mixed melting-point, ° C.*	*Weight % of higher alcohol*
2-Methyl 1-butanol	128·30	129·5	296	295	156	157	156·7	17·3
2-Methyl 1-pentanol	145·7	146·5	300	295	141	145	143	16·6
2-4-Dimethyl 1-pentanol	153·8	159–61	310	309	152–3	154–5	152–3	2·3
4-methyl 1-hexanol	162–4	165	312	309	140	144	141	3·3
2-4-Dimethyl 1-hexanol	173–5	175–80	321	323	132	. .	. .	1·0
4- or 5-Methyl 1-heptanol	180–3	182·7	327	323	133	. .	. .	0·3

to explain the formation of alcohols of high molecular weight from mixtures of carbon monoxide or carbon dioxide and hydrogen. One of the earliest suggestions was that of Fischer and Tropsch [12, 1924], who, in their early work on 'synthol', isolated and identified, besides methanol and higher alcohols, various amounts of acetaldehyde, propionaldehyde, acetone, methyl-ethyl-ketone, diethyl-ketone and methyl normal propyl ketone, as well as esters and hydrocarbons. These investigators suggested that the higher alcohols are formed by reduction of aldehydes, which result from the reduction of acids, which in their turn result from the addition of carbon monoxide to the alcohol containing one less carbon atom, thus:

$$C_2H_5OH \rightarrow C_2H_5COOH,$$
$$C_2H_5COOH \rightarrow C_2H_5CHO,$$
$$C_2H_5CHO \rightarrow C_2H_5CH_2OH.$$

This mechanism, however, only accounts for the formation of normal primary alcohols. Ketones were supposed to result from the loss of water and carbon dioxide from 2 molecules of fatty acid, thus:

$$CH_3COOH + CH_3COOH \rightarrow CH_3COCH_3 + H_2O + CO_2.$$

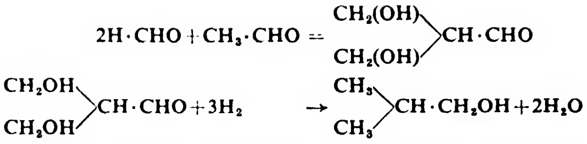
Ketones have also been regarded as dehydration products of secondary alcohols.

A more recent hypothesis concerning the formation of higher alcohols is that involving the occurrence of a series of aldol condensations starting with formaldehyde [31, 1930]. According to this scheme, 2 molecules of formaldehyde condense to give $CH_2OH\cdot CHO$, which is hydrogenated to give acetaldehyde and water. The acetaldehyde is then reduced to ethyl alcohol or then condenses with a further molecule of formaldehyde or acetaldehyde to give hydroxy-aldehydes of higher molecular weight, which would, in turn, be hydrated and reduced. The series of reactions involved are as follows:

$$2HCHO = H_2C(OH)\cdot CHO.$$
$$H_2C(OH)\cdot CHO + H_2 = CH_3CHO + H_2O.$$
$$CH_3CHO + H_2 = CH_3CH_2OH.$$
$$HCHO + CH_3CHO = CH_2(OH)\cdot CH_2CHO.$$
$$CH_2(OH)CH_2CHO + H_2 = CH_3\cdot CH_2\cdot CHO + H_2O.$$
$$CH_3CH_2CHO + H_2 = CH_3\cdot CH_2\cdot CH_2OH.$$

and so on.

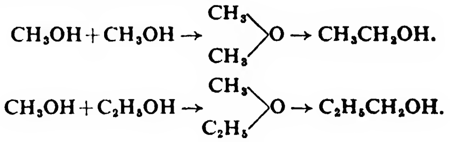
It will be noticed that according to this scheme, straight-chain alcohols should be formed. Provision is made for the production of branched-chain alcohols by a condensation involving 2 molecules of formaldehyde and 1 of acetaldehyde to give the product $(H_2COH)_2CH\cdot CHO$, which, after dehydration and reduction, would give isobutanol, thus:



$$2H\cdot CHO + CH_3\cdot CHO = \begin{matrix}CH_2(OH)\\CH_2(OH)\end{matrix}\!>\!CH\cdot CHO$$
$$\begin{matrix}CH_2OH\\CH_2OH\end{matrix}\!>\!CH\cdot CHO + 3H_2 \rightarrow \begin{matrix}CH_3\\CH_3\end{matrix}\!>\!CH\cdot CH_2OH + 2H_2O$$

The above aldol condensation mechanism for the formation of higher alcohols is widely accepted, but the non-existence of normal butanol in the products examined by Graves [19, 1931] has led this investigator to doubt its validity.

A mechanism involving progressive dehydration has also been proposed by Frolich [17, 1931], suggesting that the dimethyl ether observed to be a reaction by-product, represents an intermediate step in the production of its isomer ethanol. Similarly, methanol and ethanol would be dehydrated to ethyl methyl ether, and this would rearrange to give normal propanol, thus:



$$CH_3OH + CH_3OH \rightarrow \begin{matrix}CH_3\\CH_3\end{matrix}\!>\!O \rightarrow CH_3CH_2OH.$$
$$CH_3OH + C_2H_5OH \rightarrow \begin{matrix}CH_3\\C_2H_5\end{matrix}\!>\!O \rightarrow C_2H_5CH_2OH.$$

Frolich has also pointed out that one would expect the aldehydes to be converted to esters by addition and rearrangement. Esters have actually been isolated in higher alcohol fractions.

Similar condensations of aldehydes to higher alcohols, to give a series of aldol condensations and hydrogenations, have been assumed to explain the formation of these bodies and also higher esters in the catalytic condensation of acetaldehyde in the presence of hydrogen, carried out by Adkins, Kinsey, and Folkers [1, 1930], but, in these experiments, the yields of esters have always been greater than those of the higher alcohols.

The formation of these same higher alcohols by heating the lower alcohols with alkali has been reported by several investigators, including Guerbet [20, 1901–2], who has reported that methanol does not condense in this way but that the higher alcohols react with increasing ease. It would appear that such condensations always involve a hydrogen atom attached to the β-carbon atom, giving a series of primary alcohols, thus:

$$CH_3\cdot CH_2OH + CH_3\cdot CH_2OH \rightarrow CH_3CH_2CH_2CH_2OH \text{ (}n\text{-butanol).}$$

The above hypotheses concerning the production of higher alcohols from carbon monoxide and hydrogen have recently been critically examined by Graves [19, 1931] in the light of experience gained with the higher alcohols produced in the Du Pont Ammonia Corporation methanol plant, the compositions of which have already been given.

According to Graves the direct dehydration mechanism proposed by Guerbet (loc. cit.) offers a simple and satisfactory explanation of the formation of normal propanol, isobutanol, and 2-methyl butanol, which are present in the Du Pont product, but the presence of esters has not been demonstrated therein, although the low-boiling fractions contain traces of aldehydes and ketones. These latter compounds, however, have always been looked upon by Graves as dehydrogenation products of the alcohols rather than as residual intermediates produced by aldol condensations. The small amounts of saturated and unsaturated hydrocarbons which have been identified in the low-boiling fractions are considered to be dehydration products of the alcohols. Compared with the higher alcohols themselves, all of these other materials are only found in traces.

Graves has, therefore, proposed the following:

1. Higher primary alcohols are formed by intermolecular dehydration of two lower alcohol molecules.

2. Dehydration may involve a hydrogen atom attached to the carbon atom of methanol, thus:

(*a*) $CH_3OH+CH_3OH \rightarrow CH_3\cdot CH_2OH$.
(*b*) $CH_3\cdot CH_2OH+CH_3OH \rightarrow CH_3CH_2CH_2OH$.

but such a reaction is slow compared with one involving a hydrogen atom attached to the β-carbon atom. Thus the reactions

(*c*) $CH_3OH+H\cdot CH_2CH_2OH \rightarrow CH_3CH_2CH_2OH$ (*n*-propanol).

and

(*d*) $CH_3OH+CH_3\cdot H\cdot CH\cdot CH_2OH \rightarrow CH_3\cdot CH\cdot CH_3\cdot CH_2OH$ (isobutanol)

take place, whereas the reactions

(*e*) $CH_3CH_2CH_2OH+HCH_2OH \rightarrow CH_3CH_2CH_2CH_2OH$ (*n*-butanol)

and

(*f*) $CH_3CH(CH_3)CH_2OH+HCH_2OH$
$\rightarrow CH_3CH(CH_3)CH_2CH_2OH$ (isoamyl alcohol)

do not occur.

3. Condensation takes place with difficulty on a CH_2 group, as instanced by the failure of the reactions

(*g*) $CH_3\cdot CH_2OH+HCH_2CH_2OH \rightarrow CH_3\cdot CH_2\cdot CH_2\cdot CH_2OH$ (*n*-butanol)

and

(*h*) $CH_3CH_2CH_2OH+HCH_2CH_2OH$
$\rightarrow CH_3CH_2CH_2CH_2CH_2OH$ (*n*-pentanol)

and does not take place on a CH group, as instanced by the failure of the reaction

(*i*) $CH_3OH+CH_3CH(CH_3)CH_2OH \rightarrow (CH_3)C\cdot CH_2OH$.

Most of the higher alcohols result from a condensation on a CH_2 group.

In order to explain the formation of secondary alcohols the hypothesis is extended to include a dehydration involving a hydrogen atom attached to the carbon atom holding the OH group.

5. Raw Materials for Methanol Synthesis

Water gas is the most common source of the carbon monoxide and hydrogen used for methanol synthesis. The preparation of water gas from coke and also by catalytic processes applied to natural gases is fully described elsewhere. The relative proportion of carbon monoxide and hydrogen may be varied from those in which these gases are found in water gas, by means of the well-known water-gas catalytic process in which carbon monoxide is converted to carbon dioxide by the action of steam. The carbon dioxide may then be removed by simple water-washing. This process enables gas mixtures of any desired carbon monoxide/hydrogen ratio to be obtained, particularly those containing an excess of hydrogen. Gases containing carbon dioxide may also be employed in methanol synthesis. A recent development is the production of methanol at synthetic ammonia plants, where the methanol synthesis reaction is used as a means of carbon monoxide removal from the gas passing to the ammonia synthesis, thus partly replacing the methods of carbon monoxide removal involving scrubbing with copper-ammonium solutions or catalytic conversion to carbon dioxide. Coke oven gas is often employed as a source of hydrogen. It may also be used as a raw material for methanol synthesis, as shown by Osterreith and Dechamps [35, 1933]. The high methane content of the gas may be converted to carbon monoxide and hydrogen by well-known processes.

6. Methanol Synthesis Plant

This is fully described in the literature and, in particular, reference should be made to *The Design and Construction of High Pressure Chemical Plant*, by H. Tongue, Chapman & Hall, Ltd., London.

REFERENCES

1. Adkins, H., Kinsey, M. E., and Folkers, K. *Ind. Eng. Chem.* **22**, 1046 (1930).
2. Audibert, E., and A. Raineau. *Ann. comb. liq.* (1927); *Ind. Eng. Chem.* **20**, 1105 (1928).
3. Audibert. *Ann. comb. liq.* **6**, 655 (1931).
4. Bone, W. A. *Trans. Inst. Chem. Eng.* **8**, 102 (1930).
5. British Celanese Ltd. B.P. 300,142 (2 May 1927).
6. Brown, R. L., and Galloway, A. E. *Ind. Eng. Chem.* **20**, 960 (1928).
7. Brown, R. L., and Galloway, A. E. *Ind. Eng. Chem.* **31**, 310 (1929); **22**, 175 (1930).
8. Cryder, D. S., and Frolich, P. K. *Ind. Eng. Chem.* **21**, 867 (1929).
9. Ellis, Carleton. *Hydrogenation of Organic Substances.* 3rd ed. (D. Van Nostrand Co., Inc., 1930).
10. B.P. 227,147 (1924); 228,959 (1925); 229,714 (1925); 229,715 (1925); 231,285 (1925); 237,030 (1925); 238,319 (1925); 240,955 (1925).
11. Fischer, F., and Tropsch, H. *Brenn.-Chem.* **5**, 201, 217 (1924).
12. ——— *Die Umwandlung der Kohle in Oele*, **2**, 246 (1924).
13. ——— *Ber.* **59**, 832 (1926).
14. Francis, A. W. *Ind. Eng. Chem.* **20**, 283 (1928).
15. Frolich, P. K., Fenske, and Quiggle. *Ind. Eng. Chem.* **20**, 694 (1928).
16. Frolich, P. K. *J.S.C.I.* **47**, 176 T (1928).
17. Frolich, Per. K. *Ind. Eng. Chem.* **23**, 111 (1931).
18. G.P. 293,787 (8 March 1913); 295,202–3 (1914); F.P. 468,427; B.P. 20,488 (1915); U.S.P. 1,201,850 (1916).
19. Graves, G. D. *Ind. Eng. Chem.* **23**, 1381 (1931).
20. Guerbet. *Comp. rend.* **128**, 511, 1220 (1901); **132**, 207, 685 (1901); **133**, 300, 1220 (1901); **135**, 171–2 (1902). *Ann. Chim.* **27**, (7), 67, 105 (1902).
21. Huffman and Dodge. *Ind. Eng. Chem.* **21**, 1056 (1929).
22. *Ind. Eng. Chem.* **22**, 89 (1930).
23. Kelley, K. K. *Ind. Eng. Chem.* **18**, 78 (1926).
24. Klyukvin, Volnov, and Karpinskii. *Foreign Petroleum Technology*, **2**, 265 (1934).
25. Lazier, W. A. U.S.P. 1,746,781; 1,746,782; 1,746,783 (11 Feb. 1930).
26. Lewis, W. K., and Frolich, P. K. *Ind. Eng. Chem.* **20**, 287 (1928).
27. Marek, L. F., and Hahn, D. A. *The Catalytic Oxidation of Organic Compounds in the Vapour Phase* (Chemical Catalogue Co. Inc., 1932).
28. Mittasch, A. *Ber.* **59**, 13 (1926).
29. —— U.S.P. 1,569,775 (1926).

30. Molstad, M. C., and Dodge, B. F. *Ind. Eng. Chem.* **27**, 134 (1935).
31. Morgan, G. T. *Proc. Roy. Soc., A*, **127**, 246 (1930).
32. Morgan, G. T., Hardy, D. V. N., and Proctor, R. A. *J. S.C.I.* **51**, 1 T (1932).
33. Morgan, G. T., Taylor, R., and Hedley, T. J. *J. S.C.I.* **47**, 117 T (1928).
34. Newitt, D. M., Byrne, B. J., and Strong, H. W. *Proc. Roy. Soc., A*, **123**, 236 (1929).
35. Osterreith, J. W., and Dechamps, G. *J. Inst. Fuel*, **6**, 215 (1933).
36. Patart, G. *Chim. et Ind.* **13**, 179–85 (1925); *Bull. Soc. Enc. Industr. nat.* **137**, 141–73 (1925); *Compt. rend.* **179**, 1330 (1924).
37. Patart, G. *Proc. Intern. Conf. Bit. Coal*, 141 (1926).
38. Smith and Synthetic Ammonia and Nitrates Ltd. B.P. 275,345 (1926).
39. Synthetic Ammonia and Nitrates Ltd. B.P. 290,399 (1926).
40. Synthetic Ammonia and Nitrates Ltd. and Franklin. B.P. 293,080 (1926).
41. Synthetic Ammonia and Nitrates Ltd., Smith, and Franklin. B.P. 316,113 (1928).
42. Taylor, R. *J.C.S.* 1429 (1934).

THE SOLUBILITY RELATIONSHIPS OF MIXTURES OF GASOLINES, BENZOLES, ALCOHOLS, AND WATER

By D. A. HOWES, Ph.D., B.Sc., A.M.Inst.P.T.
Anglo-Iranian Oil Company Ltd.

THE solubility relationships of the above mixtures are of supreme importance with regard to the use of methanol and ethyl alcohol as motor-fuel components. Marketed fuels must be stable against phase separation which is liable to be caused by temperature differences and by the adventitious addition of water.

The Solubility of Methanol in Hydrocarbons and Typical Gasolines

Methanol suffers from the great disadvantage that there are few petroleum gasolines with which it is miscible in all proportions at ordinary temperatures, even when it is perfectly dry, whereas anhydrous ethyl alcohol is perfectly miscible with all gasolines at the same temperatures. This one fact limits the use of methanol as a fuel constituent very seriously and will probably prevent its use in a blended form on a large scale.

The solubility of methanol in any hydrocarbon is a function of (*a*) temperature, (*b*) the molecular configuration and physical properties of the hydrocarbon, and (*c*) the presence of water. In general, the lower the temperature the more narrow are the limits of miscibility between the two, while the presence of even very small amounts of water reduces miscibility to a very marked extent. Of the four main classes of hydrocarbons, namely, paraffins, naphthenes, aromatics, and unsaturateds, methanol is soluble to the least extent in the normal paraffins and to the greatest extent in the aromatics and is, in nearly all cases, more soluble in unsaturateds than in naphthenes. This generalization is only true, however, when comparing hydrocarbons of the same boiling-point, for in all classes of hydrocarbons, the solubility of methanol decreases with rise in the hydrocarbon boiling-point and molecular weight. Thus, methanol is more soluble, at a given temperature, in normal pentane than in normal heptane: similarly, it is more soluble in cyclohexane than in the substituted cyclohexanes and more soluble in low-boiling olefines than in high-boiling aromatics. It is also noteworthy that methanol is more soluble in branched chain-paraffins than in the normal homologues.

Table I gives some recently published figures for the solubility of methanol in hydrocarbons which support the above conclusions [7, 1933]. The fact that methanol has a lower solubility in pure normal heptane, ex *Pinus Sabiniana* [2, 1927], than in a technical grade of normal heptane is accounted for by the fact that the latter contains naphthene impurities.

From the figures given in Table I, it is evident that no definite relationship exists between the aniline point of a hydrocarbon and its solvent power for methanol. It will be noticed, however, as a very approximate guide, that, in general, the lower the aniline point, the higher the methanol solubility.

Data on the solubility of methanol in typical English market gasolines, benzole mixtures, aviation spirits, cracked spirits, &c., is given in Table II, which indicates that:

(*a*) With the exception of benzole mixtures, methanol is only soluble in gasolines to a negligible extent at a temperature of −10° C. Therefore the addition of a blending agent, or substance to promote miscibility, is always necessary.

(*b*) In the case of cracked spirits, an olefine content of 20% has a negligible effect upon methanol solubility. (This would appear contrary to the evidence given in Table I, but it is probable that the unsaturated hydrocarbons present in cracked spirit have a high average boiling-point and, consequently, have no effect upon the methanol solubility.)

(*c*) Reduction in average boiling-point causes a greater increase in methanol solubility than the presence of olefines in quantities such as are normally met in cracked spirits.

(*d*) Methanol is more soluble in benzole mixture K, which contains 53% of total aromatics and 30% of benzole

TABLE I

Solubility of Methanol in Various Hydrocarbons at −20° to +20° C.

Hydrocarbon	*Aniline point ° C.*	*Methanol solubility (% vol.)*				
		−20° C.	*−10° C.*	*0° C.*	*+10° C.*	*+20° C.*
n-Pentane*	..	3·2	4·3	7·1	12·8	Completely miscible.
Iso-pentane*	..	3·7	5·6	9·9	Completely miscible.	
n-Hexane*	57·0	2·4	3·6	5·6	9·1	24·7
n-Heptane*	68·9	0·9	1·9	3·0	4·5	6·7
n-Heptane (pure)	69·7	0·4	1·1	1·9	2·8	4·1
2,2,4-Trimethyl pentane	79·6	..	..	2·1	3·9	5·1
Cyclohexane	31·0	..		Cyclohexane crystallizes out.		
Methyl cyclohexane	41·0	..	1·4	2·1	3·1	4·1
Cyclohexane	−20·0	7·4	11·8	24·2	Completely miscible.	
Di-isobutylene	32·2	..		Miscible in all proportions.		
Octene–1 and –2 mixture	..	..	20·7	..	..	..
Trimethyl ethylene	11·0	..		Miscible in all proportions.		
Amylene mixture	14·0	..		,,		
Diethyl methyl ethylene	−40·0	..		,,		

* Impure samples.

TABLE II

The Solubility of Methanol in Various Gasolines.

	Sp. gr. 15/15° C.	*Aniline point, ° C.*	*Mid-point, ° C.*	*% Carbon*	*% Hydrogen*	*% Unsaturateds*	*% Aromatics*	*% Naphthenes*	*% Paraffins*	*Methanol solubility % vol.*	
										−10° C.	*0° C.*
English market spirit A .	0·7390	48·8	..	85·50	14·5	3·0	15·0	33·0	49·0	0·5	2·4
,, ,, B .	0·7377	46·5	120	85·41	13·93	17·0	20·0	13·0	50·0	1·0	3·85
,, ,, C .	0·7283	57·1	..	84·41	14·52	9·0	14·0	22·0	55·0	1·0	3·85
,, ,, D .	0·7334	48·2	..	84·97	14·62	3·0	12·0	41·0	44·0	0·5	2·9
,, ,, E .	0·7307	46·6	..	84·84	14·43	2·0	19·0	25·0	54·0	0·5	2·4
,, ,, F .	0·7191	52·1	..	85·19	14·24	9·0	13·0	19·0	59·0	2·4	3·4
,, ,, G .	0·7570	47·7	..	85·51	14·41	10·0	10·0	53·0	27·0	0·5	1·0
,, ,, H .	0·7559	47·7	..	85·14	14·34	12·0	10·0	49·0	29·0	0·5	1·0
Market benzole mixture K .	0·7774	20·6	..	86·92	12·55	1·0	53·0	9·0	37·0	23·7	40·2
Benzole mixture L . .	0·7609	26·7	..	..	..	6·0	36·0	23·0	35·0	15·0	43·0
Casing-head gasoline M .	0·6711	..	59	84·03	15·93	1·0	3·0	41·0	55·0	2·4	3·3
Aviation spirit N . .	0·7165	50·5	94	84·57	14·92	2·0	12·0	56·0	30·0	2·5	4·0
Cracked spirit O . .	0·7738	..	156	..	..	20·0	34·0	26·0	45·0	1·5	3·5
,, ,, P . .	0·7529	..	138	..	..	13·0	16·0	26·0	45·0	2·0	2·7
Mid-Continent straight run .	0·7388	56·3	122	..	..	4·0	9·0	35·0	52·0	0·5	2·1
California straight run .	0·7564	50·2	125	..	..	3·0	8·0	61·0	28·0	0·5	2·6
Spirit R	0·7670	30·3	112·5	85·96	13·81	3·0	26·0	55·0	16·0	2·4	3·3
,, S	0·7958	18·7	128·5	..	..	3·0	41·0	44·0	12·0	4·3	5·2
,, T	0·7786	47·0	144	..	..	nil	9·0	91·0	nil	1·0	1·0
,, V	..	−16·0	160	..	..	2·0	63·0	26·0	9·0	19·4	30·0
,, W	..	39·6	150	..	..	1·0	14·0	52·0	33·0	1·0	2·2

than in spirit V, which contains 63·2% of aromatics. The reason for this is shown later.

(*e*) Methanol has the same solubility at −10° C., in casing-head gasoline M, of mid-point 59° C. and aromatic content 2·7%, as in spirit R, which contains 25·8% aromatics. This illustrates the importance of volatility upon methanol solubility and shows that the high-boiling aromatics do not affect the methanol solubility to any marked extent.

Blending Agents for Methanol-Petrol Mixtures

Aromatic Hydrocarbons. In order to make homogeneous mixtures of methanol and gasolines, resort must be made to blending agents, substances which function in this way because of their mutual solvent power upon both methanol and gasolines. Numerous blending agents are known, but hardly any of these can be considered of commercial value because they must be used in comparatively large quantities.

As already shown, methanol is completely miscible, at ordinary temperatures, with benzene or benzole; therefore, a gasoline to which benzole has been added dissolves a greater amount of methanol than it does by itself. All other aromatic hydrocarbons act in the same way, but to greatly varying extents; their efficiency, in this direction, falling off very rapidly with rise in boiling-point and molecular weight. This is illustrated in Fig. 1, which shows the solubility of methanol at 0° C., in blends of benzene, toluene, xylene, para-cymene, and cyclohexene, with aromatic free petroleum ether of boiling range 100–120° C.

Thus, to dissolve 10% by volume of methanol in this petroleum ether, the following amounts of the hydrocarbons used as blending agents are required:

	% by vol.
Benzene	21·6
Toluene	30·0
Xylene	34·7
Para-cymene . . .	50·0
Cyclohexene . . .	37·2

Or, expressed in another way, 20% by volume blends of the hydrocarbons in the petroleum ether dissolve the following amounts of methanol (at 0° C.):

		Solubility of Methanol (% by vol.)
80% Petroleum, Ether	+20% Benzene . .	7·8
80% ,, ,,	+20% Toluene . .	4·7
80% ,, ,,	+20% Xylene . .	3·1
80% ,, ,	+20% Para-cymene .	2·3
80% ,, ,,	+20% Cyclohexene .	4·7

Benzene is, therefore, by far the most efficient blending agent of the aromatic hydrocarbons. It will be observed that the cyclic unsaturated hydrocarbon, cyclohexene, is more efficient as a blending agent than para-cymene in all concentrations up to 50%, and more efficient than xylene in all concentrations up to 35%. The relative efficiencies of the aromatic hydrocarbons as blending agents for methanol-petrol mixtures are also evident from Fig. 2.

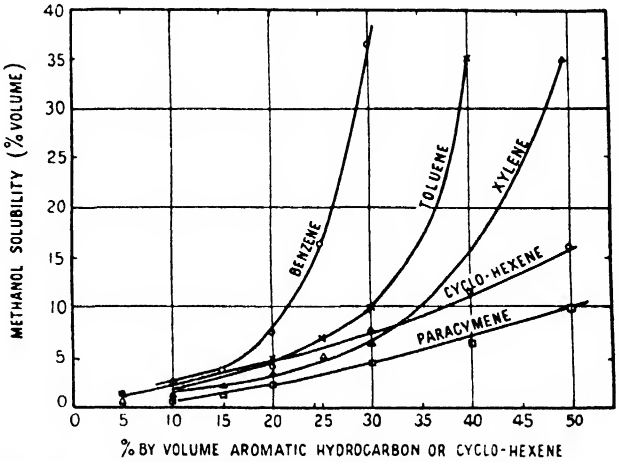


FIG. 1. Solubility of methanol at 0° C. in blends of pure hydrocarbons and petroleum ether.

Such considerations as these adequately explain why there is no definite relationship between the aromatic hydrocarbon contents of gasolines and the solubility of methanol therein.

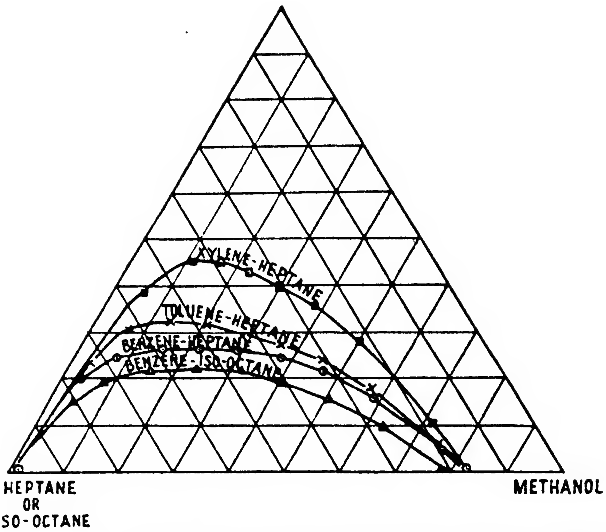


FIG. 2. Relative efficiencies of the aromatic hydrocarbons as blending agents for methanol-paraffin hydrocarbon mixtures.

The effect of temperature upon the solubility of methanol, in any gasoline, or upon the amount of blending agent required to produce miscibility, is very marked. Thus

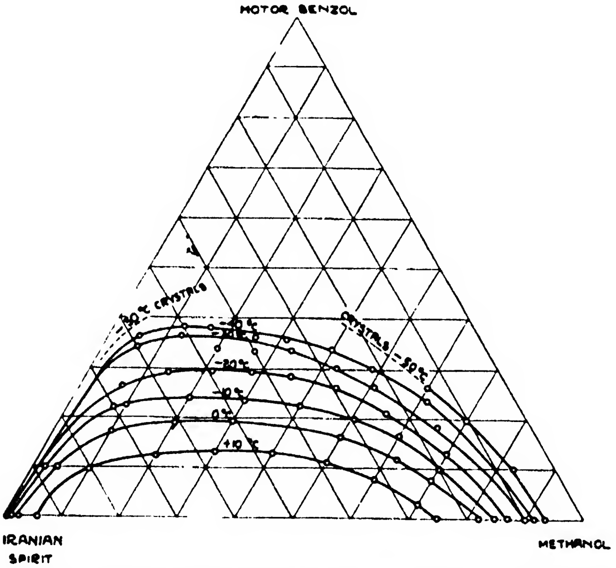


FIG. 3. Miscibility relationships of the system Iranian spirit-motor benzole-methanol at temperatures ranging from +15° C. to +50° C.

Fig. 3 shows that, in the case of an Iranian spirit, to hold 10% of methanol in solution, there is required:

9·5%	of benzole at	+15° C.
18·0%	,, ,,	0° C.
23·0%	,, ,,	−10° C.
28·0%	,, ,,	−20° C.
35·0%	,, ,,	−30° C.
38·0%	,, ,,	−40° C.

Other Blending Agents. As in the case of wet ethyl alcohol-gasoline mixtures, there are other substances much more effective than benzole in promoting the miscibility of methanol-gasoline mixtures, and substances effective in the first case are also effective in the second case. Moreover, their relative efficiencies are usually the same in each case.

The compounds most effective in this direction are the higher boiling alcohols and cyclohexanol. Anhydrous ethyl alcohol can also be used as a blending agent for methanol-gasoline mixtures, but wet alcohol is of no value in this direction. Miscibility curves for the system methanol-ethyl-alcohol-gasoline are shown in Fig. 4, in which the spirit referred to is typical of those sold on the English market during 1932.

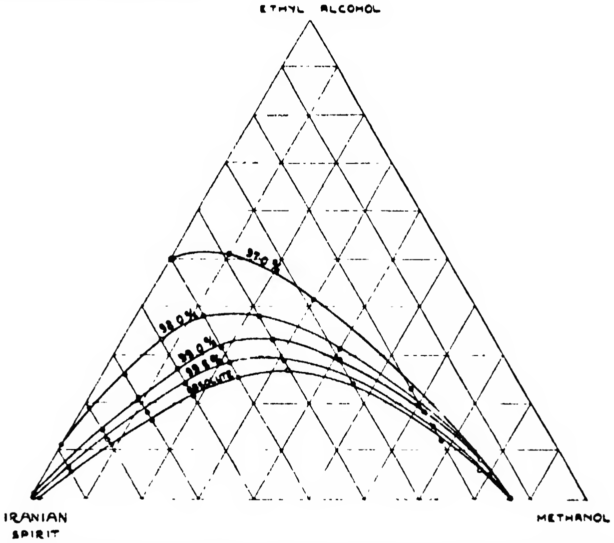


FIG. 4. Efficiency of ethyl alcohol of various strengths as a blending agent for methanol-Iranian spirit mixtures at −10° C.

Absolute ethyl alcohol has an advantage over benzole as a blending agent in that smaller quantities of it are required, and it is of interest to note, as shown in Fig. 5, that the maximum requirement of ethyl alcohol is at a methanol concentration of 40%, whereas more benzole is required to give miscibility to a 20% methanol blend than to a 40% blend.

The relative efficiencies of the higher aliphatic alcohols and other alcohols as blending agents are shown in Table III and also in Fig. 5.

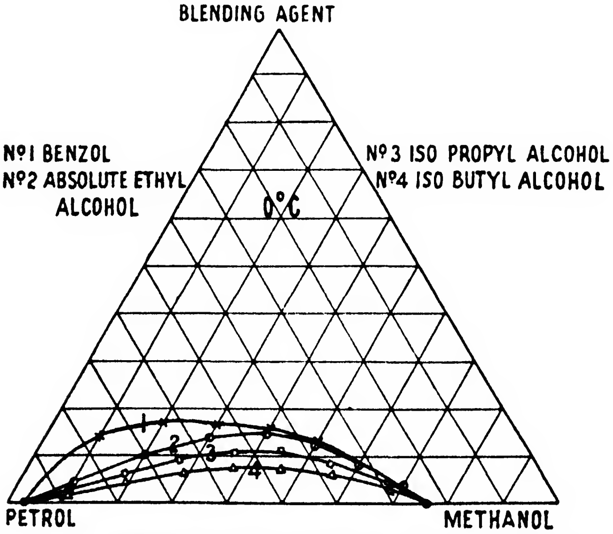


FIG. 5. Benzole and alcohols as blending agents for gasoline-methanol mixtures at 0° C.

It will be seen that the iso- and tertiary alcohols are less efficient than their normal homologues.

A point of particular interest is that the higher alcohols, such as *iso*-butanol, &c., may be produced synthetically from water gas, simultaneously and in the same plant as methanol itself; consequently, it is possible to produce in one operation a mixture of methanol and higher alcohols which is miscible with petrol.

TABLE III

The Higher Alcohols as Blending Agents for Methanol-Gasoline Mixtures [6, 1933]

(% by vol. to hold 10% of methanol in solution in a standard motor-fuel at −10° C.)

Ethyl alcohol	10·3	Synthetic fusel oil:	
n-Propyl alcohol	4·0	BP/100–200° C.	5·5
iso-Propyl alcohol	5·0	BP/200–230° C.	5·6
n-Butyl alcohol	3·5	BP/230–280° C.	6·6
iso-Butyl alcohol	4·0	BP/280–320° C.	10·6
tert-Butyl alcohol	6·0	Allyl alcohol	valueless
sec-Butyl alcohol	5·2	Phenyl-ethyl alcohol	„
n-Amyl alcohol	3·3	Benzyl alcohol	„
tert-Amyl alcohol	3·6	Cyclohexanol	3·0
n-Hexyl alcohol	3·2	*p*-Methyl cyclohexanol	3·4
n-Heptyl alcohol	3·2	*m*-Methyl cyclohexanol	3·7
n-Octyl alcohol	3·1	Howard's 'Sextol' (methy-cyclohexanol)	3·2
sec-Octyl alcohol	3·0	*α*-Terpineol	4·5
		Fenchyl alcohol	5·2

The Solubility of Ethyl Alcohol containing Water in Various Hydrocarbons and Petrols

Although absolute (i.e. water free) ethyl alcohol is miscible in all proportions with all but a very few petroleum motor fuels, ethyl alcohol containing water is only soluble to a limited extent, and blending agents are necessary as in the case of methanol-petrol mixtures. Even though absolute ethyl alcohol can be obtained in large quantities, such alcohol is hygroscopic and readily absorbs moisture from the air.

The rules governing the solubility of methanol in hydrocarbons and petrols also apply to the solubility of wet ethyl alcohol. Thus, this substance is more soluble in aromatic hydrocarbons than in naphthenes and paraffins, and more soluble in the lower members of a homologous series of hydrocarbons than in the higher members. Similarly, the lower the temperature, the lower the solubility. The effect of water in limiting the solubility of alcohol in gasoline is very marked, the addition of even so small a quantity as 1·8% being sufficient to cause marked separation. In a solution of equal parts of gasoline and absolute ethyl alcohol, the amount of the separated layer at 0° C. is as much as 36% of the volume of gasoline present.

Most of the published work on the miscibility relationships of ethyl alcohol-gasoline mixtures has been carried out using ethyl alcohol of about 95 vol.% strength, the remainder being water. This is because a mixture of ethyl alcohol and water in the proportion of 95·57 to 4·43 by weight is an azeotropic mixture of minimum boiling-point and is the mixture normally produced unless special methods of producing absolute ethyl alcohol are employed. King and Manning [9, 1929] have carried out experiments in which they determined the miscibility limits of a range of petroleum spirits with 95 vol.% alcohol, and concluded that, whilst certain petroleum spirits are fairly readily soluble (40% at −10° C.) in this alcohol, others are soluble only to the extent of about 22%. Their results, given in Fig. 6, show that Borneo straight-run benzine and, in a lesser degree, Iranian gasoline, differ from the other spirits examined in having higher solubilities.

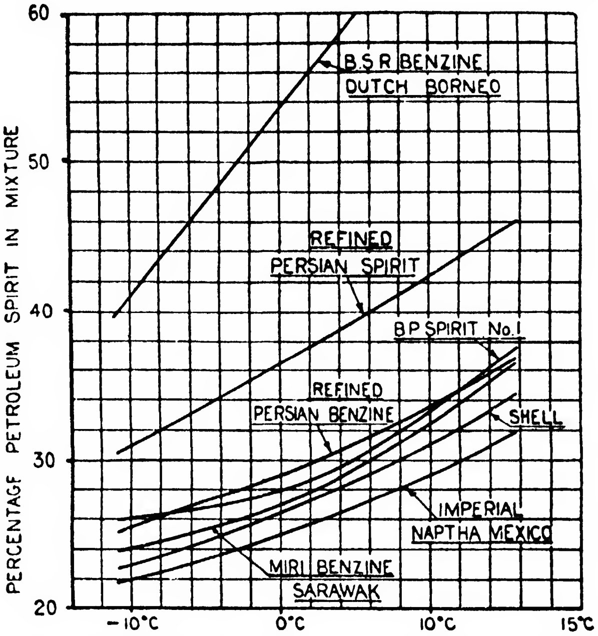


FIG. 6. The solubility of petroleum spirits in 95% ethyl alcohol.

Their solubility curves are, however, steeper, indicating that the effect of temperature is more pronounced in these two cases. Ormandy and Craven [11, 1921], have quoted similar figures for five petroleum spirits, as follows:

Origin of spirit		*Sp. gr. 15/15° C.*	*Limiting gasoline wt. % in mixture with 95% alcohol*		
			15° C.	*0° C.*	*−10° C.*
Borneo or Sumatra	(A)	0·782	77	47	37
	(B)	0·723	70	43	36
America	(E)	0·719	42	31	26
	(F)	0·704	38	28	24
Miri (Borneo)	(H)	0·767	32	25	22

The solubilities of certain hydrocarbons in alcohols of various strengths at −10° C., are as follows:

	Solubility of hydrocarbon in		
	95%	*92%*	*90% ethyl alcohol*
Isopentane	..	37	..
Pentane	..	35	..
Hexane	..	29–30	..
Heptane	..	18–22	..
„	16	..	10
Methyl cyclohexane	27	..	13

An important contribution to our knowledge on the solubility of ethyl alcohol in petroleum spirits has recently been made by Bridgeman and Querfeld [3, 1933] who have determined the solubility of alcohols of various strengths, from 99·13 to 93·21 vol.%, in gasolines of various types. These workers have found that, for straight-run spirits of the same volatility, the solution temperatures of a given blend composition differ but little from fuel to fuel, and the source of crude from which the fuel is distilled appears to have a comparatively minor effect. Cracked spirits may, however, show much lower solution temperatures than straight-run products of the same volatility. Topping a fuel of about the volatility of U.S. motor gasoline so as to reduce the 90% temperature approximately

40° C., produces a lowering in solution temperature of from 10 to 16° C. Increase of the volatility at the lower end of the distillation curve likewise produces a lowering in solution temperature. On the average the addition of 10% pentane caused a drop of 4° C.

At each constant percentage of gasoline in the blend, it was found that the logarithm of the percentage of water present (S) was a linear function of the reciprocal of the solution temperature in absolute degrees centigrade (T), so that

$$\log S = a + \frac{b}{T}.$$

Fig. 7 is taken from the figures of Bridgeman and Querfeld. This shows the differences in solution temperatures obtained with blends of 98·33% alcohol in Pennsylvanian and Californian straight-run spirits and cracked spirits of different volatilities. As already mentioned, the differences in solution temperatures are almost wholly accounted for by variations in volatility characteristics. On the other hand, one can regard straight-run Pennsylvanian gasoline having a 50% evaporated temperature of 135° C. as one of the worst spirits to use for blending with alcohol, and a cracked spirit having a 50% evaporated temperature of 96° C. as one of the most favourable for this purpose, if such highly aromatic spirits as those from certain Borneo and Sumatra crudes are excepted.

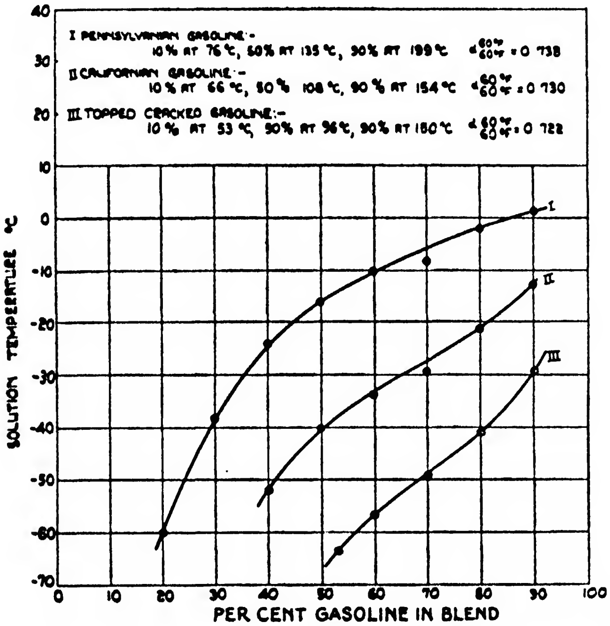


FIG. 7. Solution temperatures of blends of 98·33% ethyl alcohol in petroleum spirits of different volatilities.

The Miscibility Relationships of Ethyl Alcohol and Benzene

Absolute ethyl alcohol and benzene are miscible in all proportions at temperatures above the melting-point of the latter (5·4° C.), but as the initial freezing-point of commercial motor benzole is about −11° C., such mixtures are susceptible to crystallization only when pure benzene is used. The freezing-points of mixtures of pure benzene and absolute alcohol are such that, at a temperature of −10° C., the maximum amount of benzene permissible in a stable solution is about 40%; of commercial benzole the proportion is much greater.

Ethyl Alcohol-Gasoline-Benzole Mixtures

Interesting data on this ternary system, using 94 to 98% ethyl alcohol, have been published by King and Manning [9, 1929]. Their results indicate that the particular gasoline used (sp. gr. 15/15° C., 0·743; 39% distillate at 100° C.; end point 190° C.), is soluble in alcohols of various strengths to the following extents at 10° C. and 0° C.

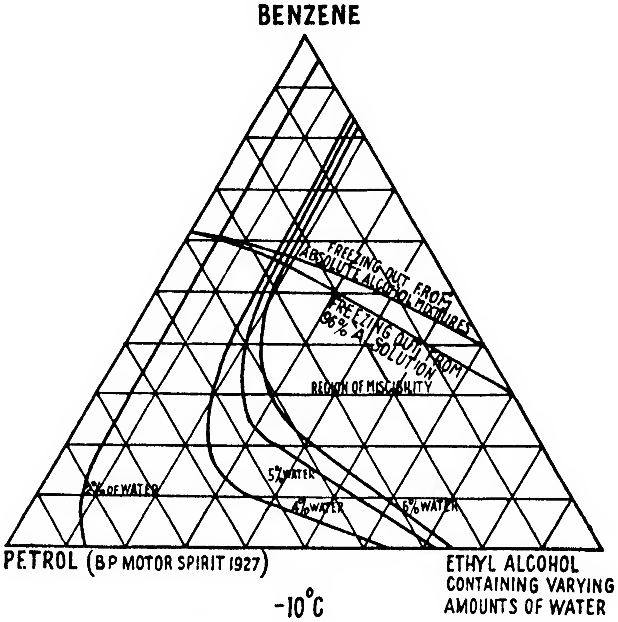


FIG. 8. The system gasoline-benzene-ethyl alcohol containing varying amounts of water.

	10° C. %	*0° C.* %
94% ethyl alcohol . .	30·0	27·0
95 „ „	43·0	33·0
96 „ „ . . .	66·0	46·0
98 „ „ . . .	95·0	94·0

The necessity of using absolute ethyl alcohol in blends with gasoline is obvious from these figures. Fig. 8, which is reproduced from King and Manning's paper, shows a large area of immiscibility even when 98% alcohol is used with pure benzene. Alcohol of this strength is not even miscible with pure benzene in all proportions at −10° C., much less can any mixture with benzene be made to mix with petrol in all proportions. The limits of miscibility with motor benzole are even less.

With regard to blending agents for aqueous ethyl alcohol-gasoline mixtures, it is a general rule that those substances found effective in promoting miscibility in methanol-gasoline mixtures are also effective in the case of ethyl alcohol blends and the relative efficiencies of such compounds are usually the same in both cases. Ormandy and Craven [12, 1923] found in 1923 that when a small proportion of the alcohol was replaced by an equal volume of any one given blending agent the change in separation temperature Δt was proportional to the volume of blending agent added, and inversely proportional to the volume of alcohol originally present, within certain limits. Thus, if B = % by volume of blending agent replacing an equal volume of alcohol and $A = \%$ by volume of alcohol before replacement, then

$$\Delta t \propto \frac{1}{A}$$

$$\Delta t \propto B$$

$$\text{or } \Delta t = K\frac{B}{A}.$$

The constant $K = \frac{\Delta t A}{B}$ might be called the 'blending power' of the blending agent, and when positive indicates that such an agent has a positive action in assisting miscibility. The value of K is not rigorously constant over a range of alcohol concentrations, but is sufficiently so to give an idea as to the relative value of a blending agent. Values for a series of blending agents on this basis are given in Table IV.

Ormandy and Craven state that no substance so far examined is more than one-fifth part as effective in preventing separation as water is in bringing it about, and it is extremely unlikely that any such substance will be found. The truth of such a prediction has been fully demonstrated during the past few years when, in spite of many attempts, no really successful blending agent has yet been found.

TABLE IV

Relative Efficiencies of Various Blending Agents in promoting Miscibility

In a mixture consisting of 85% hydrocarbons, 10% of 95% alcohol, 5% blending agent.

	$K = \frac{\Delta t A}{B}$	
	Heptane	*Gasoline*
Benzene	3	1
Toluene	−6	..
m-Xylene	−18	..
Turpentine	0 (about)	>0
Heptane	−11	..
Cresol	123	114
Aniline	51	26
Methyl alcohol	−24	−30
Ethyl alcohol 95%	0	0
,, 100%	72	72
Propyl alcohol	90	70
Butyl alcohol	168	144
Amyl ,,	170	150
Hexyl ,,	47	..
Ether	small	3
Acetone	41	18
Ethyl acetate	small	27
Cyclohexanol	201	150
Acetaldehyde	−20	..
Water	−1,000	..

Patented Blending Agents for Alcohol-Gasoline Mixtures

The most diverse substances have been patented as blending agents for alcohol-gasoline mixtures, some of which are very effective and some, of course, of very little value. Examples are anhydrous fusel oil or amyl alcohol [1, 1916], camphor, pine tars or pine-tar products [5, 1917], aromatic hydrocarbons [14, 1919], carbon disulphide [15, 1919], and fatty acids, such as ricinoleic acid or castor oil [16, 1919]. Complex ketones [13, 1926] have been protected and, despite their bad odour, strongly basic aliphatic amines, such as triethyl amine, benzylamine or piperidine [10]. The I.G. have proposed the use of alkyl formates for a similar purpose [8, 1931].

The Stability of Alcohol Fuels to Water Additions

Because the lower aliphatic alcohols, methanol, and ethyl alcohol, are miscible with water, fuels containing these substances are capable of dissolving small amounts of water. When, however, more than a small quantity of water is added to an alcohol-gasoline mixture, it causes a separation into two immiscible layers, the lower one of which consists essentially of alcohol and water and the upper layer consists mainly of hydrocarbons. This property is by far the most objectionable feature of alcohol fuels and, in this respect, methanol mixtures are less satisfactory than ethyl alcohol blends. Under storage conditions, i.e. in tanks, the advantage is obviously all in favour of those fuels, e.g. gasoline, that are quite immiscible with water, since, if such fuels become contaminated with water, the water can be easily separated off and the composition of the fuel is not affected. On the other hand, if the fuel can be delivered to the tank of an automobile without being contaminated with water, then the advantage lies with the type of fuel which will dissolve small amounts of water. The subsequent addition of quantities of water, less than that required to cause separation, does not affect the running of the engine, whereas, with fuels that do not dissolve water, the same small amounts of water lead to erratic running and even stoppage of the engine. Such water is normally deposited in the carburettor float-chambers and fuel-line systems of automobiles and frequently causes trouble, but when alcohol fuels are used, this trouble is no longer experienced.

Alcohol fuels intended for use in automobiles must, therefore, have a high 'water tolerance', i.e. they must be capable of dissolving large amounts of water without separating into two immiscible layers. Defining 'water tolerance' in this way, it follows that the amount of water which can be added to an alcohol blend before separation occurs depends upon the following factors.

1. The nature of the alcohol or alcohols present.
2. Temperature.
3. Alcohol content of the blend.
4. Excess of blending agent present.

The effects of temperature upon the miscibility relations of alcohols and gasolines have already been pointed out, and it follows from this that the lower the temperature the lower the water tolerance of any alcohol blend. The effect of excess blending agent is also obvious, but blending agents that are miscible with water confer to alcohol blends containing them a higher water tolerance than those which are immiscible with water. In other words, of two alcohol-gasoline blends, both containing the same amount of alcohol and having the same cloud-point or separation temperature, one of which contains a water-soluble blending agent and the other a blending agent that is immiscible with water, the former has the higher water tolerance.

The effect of the alcohol content of a blend upon its water tolerance is evident from Fig. 9, which refers to gasoline-benzole-methanol mixtures, and shows that blends rich in methanol will dissolve up to 8% by volume of water at 0° C., without causing separation (i.e. 360 c.c. of water per gal.), whereas blends containing small amounts of methanol are capable of dissolving less than 0·1% of water (i.e. 4·5 c.c. per gal.). Fig. 10 also shows the effect of excess blending agent upon water tolerance.

The effect of temperature upon the water tolerance of a benzole-gasoline methanol blend is pronounced. In the case of a 10/30/60 methanol-benzole-gasoline blend at a temperature of +15° C., no less than 6 ml. of water is capable of dissolving in each gallon of fuel mixture without causing separation, whereas, at −10° C., the water tolerance is reduced to 2 c.c. per gal. (i.e. 0·04%).

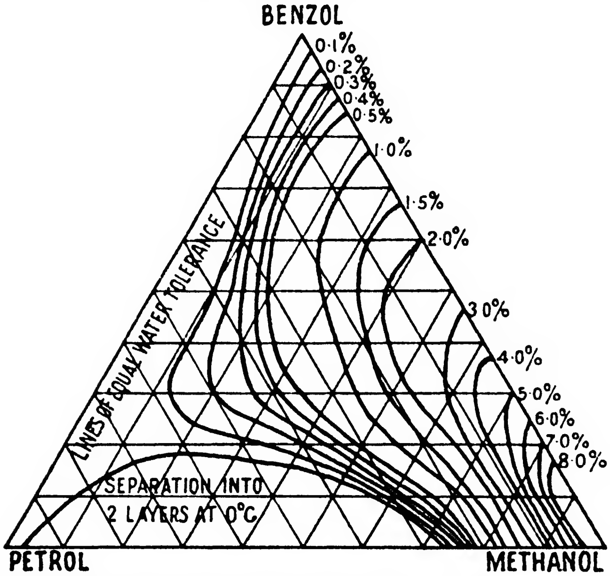


FIG. 9. Water tolerances of gasoline-benzole-methanol mixtures at 0° C.

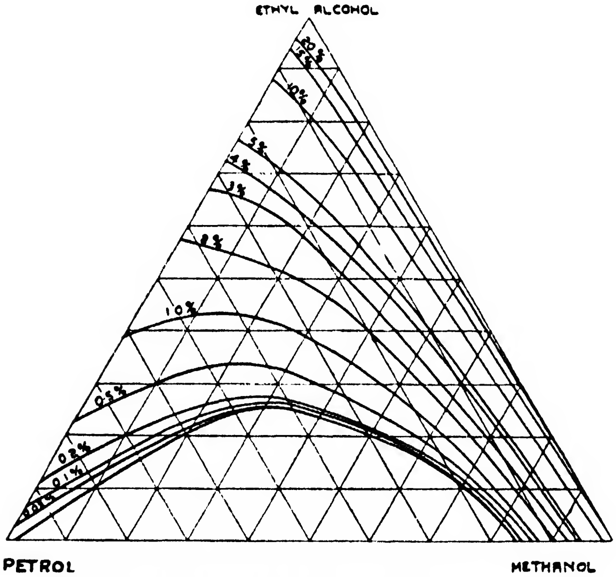


FIG. 10. Water tolerances of gasoline-ethyl alcohol-methanol mixtures at −10° C.

Ethyl alcohol is particularly valuable as a blending agent for methanol-gasoline mixtures because blends containing an excess above that necessary to give miscibility have a higher water tolerance than mixtures containing benzole as a blending agent. This is evident from Fig. 10, which shows the water tolerances of mixtures of gasoline-methanol-absolute ethyl alcohol at −10° C.

A comparison of the water tolerances of ethyl alcohol blends and methanol blends is made possible by the data of Dumanois [4, 1931] referring to the former. This is plotted in Fig. 11 together with values for a methanol-benzole-gasoline blend containing 30% of benzole.

It is evident that, for the same alcohol concentrations, ethyl alcohol blends have much higher water tolerances than methanol blends for alcohol concentrations of up to 50%. This graph, however, does not give a fair comparison because the methanol blends referred to contain 30% of benzole, which favourably influences their water tolerances. A better comparison is shown in Fig. 12, which refers to mixtures of methanol and ethyl alcohol with benzene, from which it is evident that a 40% ethyl alcohol blend in benzene has a water tolerance more than double that of a 40% methanol blend.

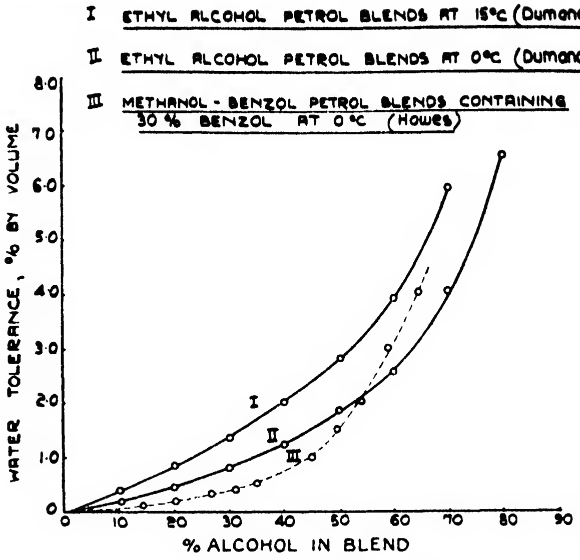


FIG. 11 Water tolerances.

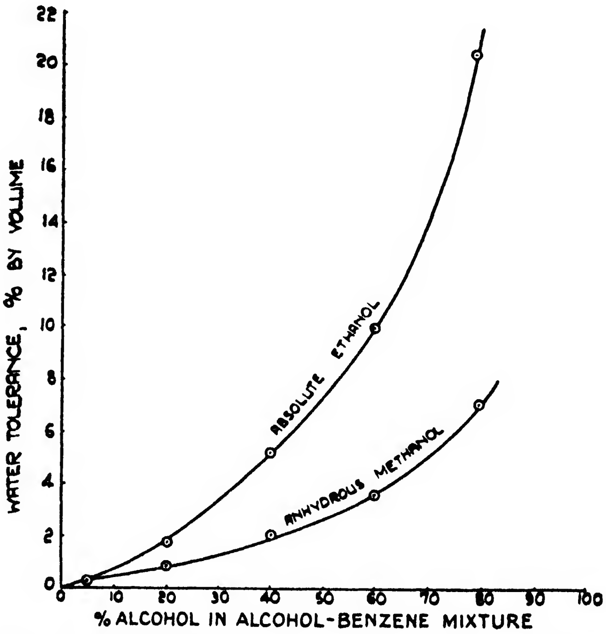


FIG. 12. Water tolerances of benzene-ethyl alcohol and benzene-methanol mixtures at 0° C.

It will be evident from the above considerations that, although an alcohol blend may be quite stable in itself at the temperatures to which it is subjected in use, and even though it may be capable of dissolving small amounts of water without suffering disintegration, it may be separated into two layers by the addition of gasoline. This is most prone to occur in the case of alcohol fuels stabilized by the addition of blending agents which are not soluble in water and occurs more readily with methanol blends than ethyl alcohol blends. Thus, referring to Fig. 9, to hold 10% of methanol in solution in a blend with gasolines at 0° C., 14% by volume of benzole is necessary, but if this is diluted with an equal volume of gasoline, reducing the benzole concentration to 7%, the fuel is separated into two layers. It is, therefore, necessary in practice to employ a considerable excess of blending agent so that dilution with gasoline may not bring about separation and so that an adventitious addition of water may not cause the same result. When such precautions are taken, alcohol blends can be used with complete satisfaction and no trouble from separation is experienced. A 10% methanol blend in gasoline stabilized by the addition of benzole has been described [7, 1933] which was stable at all temperatures down to −28° C., and which had a water tolerance of 3·5 c.c. per gal. at 0° C. This blend was on sale for over a year and gave no trouble due to separation, either by water addition or dilution with gasoline.

With regard to the reported hygroscopicity of alcohol fuels and the resulting danger of separation, the experiences which have been reported [7, 1933] suggest that methanol blends may be used over prolonged periods without any trouble from this cause. It is true that, under laboratory conditions, alcohol-gasoline blends absorb water vapour from the air when freely exposed to the latter and eventually separate into two layers, but, in actual practice, motor fuels are not freely exposed to the atmosphere and, as a result, can often be used with satisfaction. However, it is agreed that the presence of a water-soluble substance in gasolines is a potential source of much trouble.

The necessity of using anhydrous, or very nearly anhydrous, alcohols in the production of alcohol fuels is, of course, essential because the lower the water content of the alcohol used, the greater is the general physical stability and water tolerance of the blended fuel, and, moreover, the blending-agent requirements are reduced. Fortunately, methanol can be produced in an anhydrous state fairly easily, simple distillation alone being necessary, but with ethyl alcohol this is rather more difficult because of the formation of the azeotropic mixture with water. Nevertheless, ethyl alcohol containing not more than 0·5 to 0·8% of water is now produced in quite large quantities in England and in Europe.

REFERENCES

1. Axtell, F. C. B.P. 109,806 (5 Sept. 1916).
2. Brame, J. S. S., and Hunter, T. G. *J.I.P.T.* **13**, 794 (1927).
3. Bridgeman, O. C., and Querfeld, D. *Ind. Eng. Chem.* **25**, 523 (1933).
4. Dumanois, P. *Rev. Petr.* (1931).
5. Flint, T., and Brown, F. G. B.P. 111,661 (7 Sept. 1917).
6. Gordon, K. *Proc. World Petr. Cong.* London, **2**, 788 (1933).
7. Howes, D. A. *J.I.P.T.* **19**, 301 (1933).
8. I.G. Farbenind. A.-G. F.P. 725,405 (29 Oct. 1931).
9. King, J. G., and Manning, A. B. *J.I.P.T.* **15**, 350 (1929).
10. Lantz, V. U.S.P. 1,869,486.
11. Ormandy, W. R., and Craven, E. C. *Proc. Inst. Auto. Eng.* **16**, 143 (1921).
12. —— —— *J.I.P.T.* **9**, 36 (1923).
13. Soc. Le Franc et Cie. F.P. 622,077 (3 Apr. 1926).
14. U.S. Industrial Alcohol Company. B.P. 128,915 (16 June 1919).
15. —— B.P. 133,709 (10 Oct. 1919).
16. —— B.P. 134,766 (30 Apr. 1919); B.P. 136,452 (8 May 1919).

SPECIAL PRODUCTS
DI-ISOBUTENE AND ISO-OCTANE

By S. F. BIRCH, Ph.D., and T. TAIT, Ph.D.
Anglo-Iranian Oil Company Ltd.

ISOBUTENE was first polymerized by Butlerov [2, 1876–8], who obtained the dimers by heating isobutene or tertiary butyl alcohol with sulphuric acid in a sealed tube.

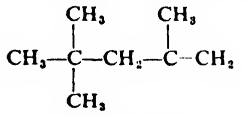
The polymerization of isobutene may be effected both thermally and with the aid of catalysts, but the former method tends to give products other than polyisobutenes, including paraffins and naphthenes [13, 1929]. Catalytic polymerization of isobutene, however, proceeds readily and very smoothly, the products formed being determined by the vigour of the catalyst and the conditions employed. Thus boron trifluoride [3, 1873; 22, 1927] and aluminium chloride [27, 1921] lead to the formation of high molecular weight oils, although if the latter reagent is used in the form of a double complex with such a compound as diphenyl sulphone, the vigour of the action is so diminished that appreciable amounts of the di- and tri-merides are obtained [1, 1931].

Polymerization can also be effected by means of certain activated earths such as floridin, a reaction which has been investigated by Lebedev and Koblianski [19, 1930], van Winkle [33, 1928], and Lebedev and Filonenko [18, 1925]. The first of these investigators found that at −80° C. polymerization proceeded with quite a high velocity, while at 200° C. it was much retarded. They observed that a considerable evolution of heat—heat of polymerization—took place and that the formation of lower boiling polymers was favoured by passing gaseous isobutene over floridin at room temperature with removal of the products as formed. Fractionation of the liquid polymers gave compounds up to the heptameride. This reaction is of particular interest in showing a definite degree of reversibility, for in later experiments [19, 1930] the same investigators found that passage of the higher polymers over floridin at 200° C. resulted in depolymerization with the formation of lower polymers and isobutene. Of the polymers examined di-isobutene proved to be the most stable and the least susceptible to depolymerization.

When the lower polymerides are required, however, polymerization is most conveniently effected by acid catalysts either in the liquid phase, e.g. sulphuric acid, or in a supported form, e.g. orthophosphoric acid on charcoal. Numerous investigators, following upon Butlerov's early experiments, have examined the reaction of isobutene with sulphuric acid, and to-day considerable quantities of di-isobutene are being prepared technically by this method.

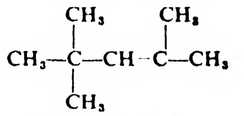
The reaction with liquid-phase catalysts definitely takes place in two stages, absorption of the isobutene with subsequent hydration to tertiary butyl alcohol being followed by dehydration and polymerization. As the acid employed must be capable of performing the functions of hydrator, dehydrator, and polymerizer, the concentration is obviously a matter of considerable importance. Thus Butlerov [2, 1876–8] in his classical research found that with sulphuric acid of comparatively low concentrations—50% and even lower—hydration of the olefine took place at room temperatures, but at 100° C. di-isobutene was formed. With 80% acid, however, polymerization occurred in the cold and tri-isobutene formed the main product. Nef found that more concentrated acid yielded even higher polymers. The question of acid concentration is more fully discussed at a later stage. The reaction may also be carried out using liquid phosphoric acid in place of sulphuric acid. Thus, using 100% acid in a rotating autoclave, Ipatiev [14, 1935] has shown that polymerization can be effected over a wide temperature range. Polymer produced at 30° C. contained only two individuals, di- and tri-isobutenes, while that formed at 130° C. apparently contained seven. The increased complexity of the product formed at the higher temperature indicates either that isomerization occurs or that there is variation in the way in which the elements of phosphoric acid are removed from the intermediate esters. By replacing liquid phosphoric acid with the acid supported on an inert carrier, e.g. active charcoal, kieselguhr, &c., similar results may be obtained, the increase in the complexity of the product with rising temperature being then most marked.

Little was known of the chemical constitution of isobutene polymers until comparatively recently, when in 1932 McCubbins and Adkins [20, 1930] proved by ozonization that di-isobutene contained two compounds, 2,4,4-trimethylpentene-1 and 2,4,4-trimethylpentene-2, the former being present in greater amount in the ratio 4:1.



$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\overset{CH_3}{C}-CH_2$

2,4,4-trimethylpentene-1



$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH-\overset{CH_3}{C}-CH_3$

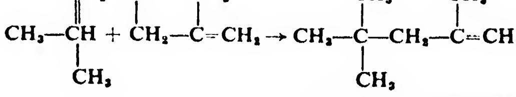
2,4,4-trimethylpentene-2

Later Whitmore and his co-workers [26, 1932; 28, 1932; 30, 1931], by careful fractionation, succeeded in isolating and examining the individual hydrocarbons; they showed that the pentene-1 was the lower boiling isomer, a fact which McCubbins and Adkins [20, 1930] had been unable to ascertain. The physical properties of the two isomers obtained by Tongberg, Pickens, Fenske, and Whitmore [26, 1932] are given in the following table.

TABLE I

Isomer	*Boiling-point (corrected) at 760 mm.*	d_4^{20}	n_D^{20}	*Freezing-point ° C.*
2,4,4-trimethyl-pentene-1 .	101·2	0·7151	1·4082	−93·6±0·1
2,4,4-trimethyl-pentene-2 .	104·5	0·7211	1·4158	−106·5±0·1

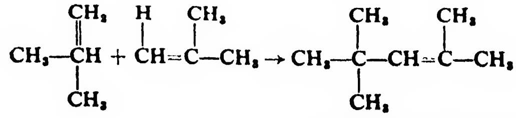
The mode of formation of these compounds cannot yet be regarded as satisfactorily proved. Schematically the reaction may be represented as follows:



$CH_3-\underset{CH_3}{\overset{CH_2}{\overset{\|}{C}H}} + \overset{H}{C}H_2-\overset{CH_3}{C}=CH_2 \rightarrow CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\overset{CH_3}{C}=CH_2$

2,4,4-trimethylpentene-1

and

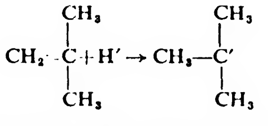


$CH_3-\underset{CH_3}{\overset{CH_2}{\overset{\|}{C}H}} + \overset{H}{C}H=\overset{CH_3}{C}-CH_3 \rightarrow CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH=\overset{CH_3}{C}-CH_3$

2,4,4-trimethylpentene-2

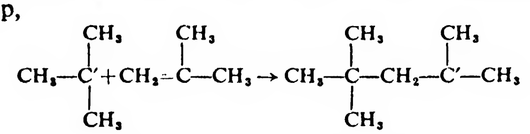
Kondakov [17, 1893, 1896] suggested for the mechanism of the reaction the formation of an intermediate compound tertiary butyl sulphuric acid, which, being extremely unstable, decomposed immediately. While tertiary alkyl sulphuric acids of this type have never been isolated in the pure state or even as salts in the case of the lower members, there is actually little doubt that they exist momentarily at least under favourable circumstances. The fact, for example, that esterifications with isobutene are possible in the presence of sulphuric acid is proof of their formation. The writers have also observed that tertiary butyl alcohol forms a white crystalline solid when treated with liquid phosphoric acid (89%). This solid, which possesses a melting-point near that of phosphoric acid (100%), can be melted without decomposition, but decomposes when warmed above its melting-point to give polymer and regenerate the acid. It may be a phosphoric acid ester corresponding to Kondakov's sulphuric acid ester or an addition compound.

Several theories have been advanced to explain the formation of the two dimers. There is, of course, a possibility of one being derived from the other by secondary change but it appears more likely that both arise as a consequence of the normal mechanism controlling polymerization. The two most recent theories are those of Whitmore [28, 1934] and of Kline and Drake [16, 1934]. Whitmore's theory for polymerization by acid catalysts is based on the catalytic effect of hydrogen ions present in the reaction mixture. The first step consists in the addition to a molecule of isobutene of a hydrogen ion with the formation of a positively charged *tert*-butyl group. The same active group is obtained by the action of acid on *tert*-butyl alcohol.



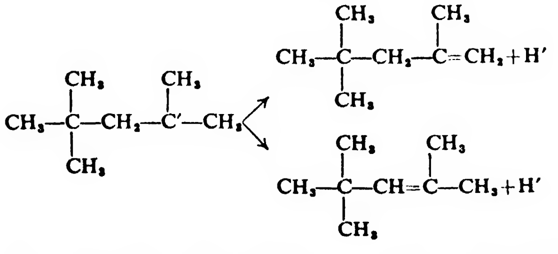
$$CH_2{=}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}+H' \rightarrow CH_3{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C'}}$$

The activated tertiary butyl group is now capable of combining with a molecule of isobutene in the same way as the hydrogen ion, yielding an activated intermediate group,



$$CH_3{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C'}}+CH_2{=}\overset{\displaystyle CH_3}{C}{-}CH_3 \rightarrow CH_3{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}{-}CH_2{-}\overset{\displaystyle CH_3}{C'}{-}CH_3$$

which may lose a hydrogen ion in two different ways, to give the two isomers of di-isobutene



$$CH_3{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}{-}CH_2{-}\overset{\displaystyle CH_3}{C'}{-}CH_3 \begin{cases} \nearrow CH_3{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}{-}CH_2{-}\overset{\displaystyle CH_3}{C}{=}CH_2+H' \\ \searrow CH_3{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}{-}CH{=}\overset{\displaystyle CH_3}{C}{-}CH_3+H' \end{cases}$$

The mechanism of polymerization proposed by Kline and Drake is rather different in conception. It is based upon a theory somewhat analogous to that put forward by Rice [24, 1931] for the thermal decomposition of organic compounds from the standpoint of free radicals. On this theory isobutene behaves as if it were activated in two ways, $CH_3^- \, {}^+C(CH_3){=}CH_2$ and $H^+ \, {}^-CH{=}C(CH_3)_2$. From considerations of the relative strengths of the C—C and C—H bonds it is to be expected that isobutene will be predominantly activated as $CH_3^- \, {}^+C(CH_3){=}CH_2$. Polymerization is then supposed to proceed by the addition of the activated fragments to the double bond of a second molecule of isobutene and the existence of two dimers is explained by this dual activation. The ratio of 4:1 found experimentally for the dimerides is accounted for by the greater tendency of the activation to proceed in one direction.

While tri-isobutene might be anticipated to contain relatively large numbers of isomeric dodecenes, Whitmore [28, 1934] believes that four predominate.

$(CH_3)_3{\cdot}C{\cdot}CH{=}C(CH_3){\cdot}CH_2{\cdot}C(CH_3)_3$
2,2,4,6,6-pentamethylheptene-3

$\{(CH_3)_3{\cdot}CH_2\}_2C{=}CH_2$
Unsym. di-isopentylethylene

$(CH_3)_3{\cdot}C{\cdot}CH_2{\cdot}C(CH_3)_2{\cdot}CH_2{\cdot}C(CH_3){=}CH_2$
2,4,4,6,6-pentamethylheptene-1

$(CH_3)_3{\cdot}C{\cdot}CH_2{\cdot}C(CH_3)_2{\cdot}CH{=}C(CH_3){\cdot}CH_3$
2,4,4,6,6-pentamethylheptene-2

He makes no mention, however, of the relative proportions in which the isomers are present. Their formation is explained by the addition of the activated intermediate group—which normally loses a hydrogen ion to form di-isobutene isomers—to isobutene or by the addition of an activated *tert*-butyl group to one or other of the two dimers. The trimers are then formed by loss of a hydrogen ion from these secondary activated intermediate groups. According to Kline and Drake [16, 1934] six isomeric trimers are to be expected, but since four are derived from the predominating dimer, it is obvious that these would predominate in tri-isobutene.

As is to be expected from their branched structures, both dimerides and trimerides possess relatively high octane values. Campbell, Lovell, and Boyd [4, 1931] examined the individual dimers in their engine and obtained the following results:

TABLE II

Isomer	*Blending octane number*
2,4,4-trimethylpentene-1 . .	150
2,4,4-trimethylpentene-2 . .	144

These values were deduced from aniline equivalents determined in 20% concentration in a 50 octane number base blend using a jacket temperature of 100° C. Some doubt must be cast upon values determined in this way, for di-isobutene when examined in blend in a C.F.R. engine using motor-method conditions does not show a straight-line relationship between concentrations and octane number, but a very definite decrease in blending value with concentration. Tri-isobutene gives similar results, and it follows that any value for the pure hydrocarbons based upon determinations carried out in 20% blend can only give comparative results (Fig. 1).

The tendency of the polyisobutenes to depolymerize at elevated temperatures in the presence of floridin has already been mentioned. Depolymerization is quite marked, even in the absence of a catalyst at 300° C., and increases rapidly with increasing temperature. In the presence of silica gel it is considerable above 250° C., both the di- and trimerides largely being converted to isobutene. The possibility of utilizing depolymerization as a means for converting high-boiling polyisobutenes into the more valuable dimeride is suggested in an I.G. patent [13], depolymerization being effected by an aluminium oxide catalyst between 200° and 300° C.

Commercial Production of Di-isobutene.

Commercially, di-isobutene is produced by the sulphuric acid polymerization of isobutene. The operation is carried out in three stages: (1) segregation of isobutene into a narrow C_4 fraction by distillation, (2) treatment with sulphuric acid to remove the isobutene as tertiary butyl alcohol and (3) heat treatment of the separated acid layer to bring about dehydration of the alcohol and polymerization of the isobutene. During this operation the acid is recovered at its original concentration and after cooling is ready for further use.

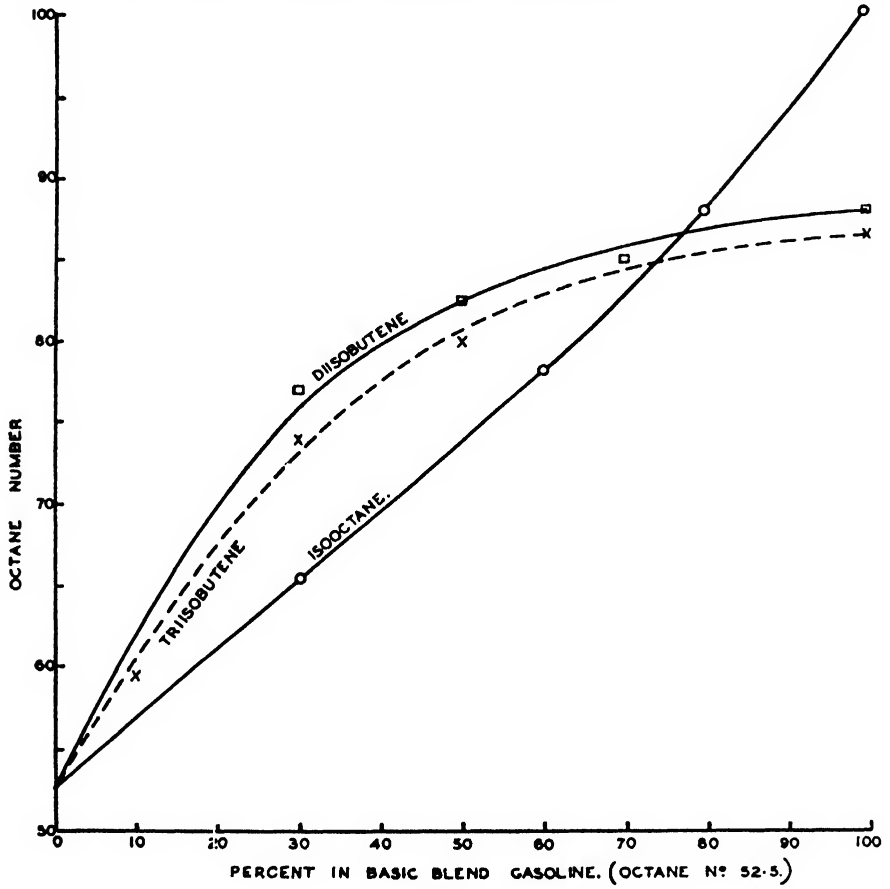


FIG. 1.

Raw Feed.

With normal refinery operation isobutene derived from cracking processes is found both in the cracking gases and in the gasoline. Since the vapour pressure of the gasoline marketed is determined by summer and winter conditions, the volume and composition of the gas leaving the stabilizer varies with the season of the year. This fact is well illustrated by the following analyses given by Egloff [10, 1936] Although the amount of isobutene varies, it would be possible, if the demand for it proved sufficiently great, to stabilize to such an extent that the isobutene normally left in the gasoline was completely recovered.

TABLE III

Stabilizer Gas Analyses

	Winter operation Mol. %	*Summer operation Mol. %*	*Yearly average Mol. %*
Methane	0·89	0·51	0·70
Ethylene	1·24	0·70	0·97
Ethane	9·96	5·60	7·78
Propene	21·08	11·88	16·48
Propane	49·10	27·80	38·45
Isobutane	8·25	16·45	12·35
Isobutene	5·05	7·91	6·48
n-Butenes	3·91	13·15	8·53
n-Butane	0·52	16·00	8·26

Early patents proposed the treatment of cracked gases in the vapour phase without previous concentration of isobutene but under these conditions, with the concentrations of acid usually recommended, absorption is slow and incomplete. Although the use of an isobutene concentrate would undoubtedly prove beneficial, it is more convenient to conduct the process entirely in the liquid phase, where the advantage of a C_4-cut becomes threefold. The highest isobutene concentration possible reduces materially the size of the plant (an important consideration as it must be constructed of acid-resisting material), more efficient removal of isobutene is possible, and the absence of more volatile hydrocarbons results in a lower vapour pressure with further saving in cost as less robust construction is required.

The C_4-fraction is most conveniently obtained as a tray cut from a stabilizer column, and the following approximate analysis is typical of a cut obtained in this way.

TABLE IV

Hydrocarbon	*% by volume*
Isobutene	21
Butenes	44
Butanes	24
Butadiene	11

When sulphur removal is considered desirable it is easier to remove it from the feed stock than from the crude di-isobutene, and the removal may conveniently be accomplished by thorough washing with dilute caustic soda or lime water. The sulphur is present mostly as low molecular weight mercaptans and these, owing to their relatively acidic nature, can be effectively extracted (see article on Refining).

Isobutene Absorption.

As mentioned above, the concentration of the sulphuric acid employed is of considerable importance in determining the course of the reaction. While medium concentrations readily effect hydration of the olefine, stronger acid results in immediate polymerization accompanied by charring and consequent fouling of the acid. As the acid/isobutene ratio used is high, it is desirable to recover the acid in as clean a condition as possible in order that it may be recycled without further treatment. Furthermore, while the acid must be sufficiently strong to effect reasonably rapid absorption of the isobutene, it must fall short of the concentration at which the other olefines present begin to react. In practice, as it is impossible to fulfil this last condition entirely, it is important to reduce reaction with olefines other than isobutene as far as possible since the alkyl sulphuric acid derived from the *n*-butenes is not easily decomposed under the conditions usually employed in the process. This would result in the progressive accumulation of butyl sulphuric acid in the acid and a tendency for the product to become contaminated with *sec*-butyl alcohol and di-*sec*-butyl ether. Fortunately isobutene is by far the most reactive olefine present. This is well illustrated by the following figures for the three butenes calculated by Davis [7, 1928] from Michael and Brunel's data [21, 1909].

TABLE V

Olefine	*Acid conc.* %	*Temp.,* ° *C.*	*Absorption coeff. K*
Isobutene (pure) . .	58·6	28–9	105×10^{-3}
„ (51·8%) .	58·6	28–9	75×10^{-3}
2-Butene (pure) . .	58·6	28–9	$0{\cdot}54\times10^{-3}$
„ „ . .	76	29–30	$10{\cdot}0\times10^{-3}$
1-Butene (pure) . .	76	29–30	$5{\cdot}0\times10^{-3}$

The relative rates of absorption by sulphuric acid are, therefore,

1-Butene = 1
2-Butene = 2
Isobutene = 280–390

It was shown by Dobryanski [8, 1925] that butadiene is absorbed by 63% sulphuric acid at a rate intermediate between those of isobutene and the normal butenes, but nearer to the latter. It therefore follows that, provided an acid concentration is chosen of which the rate of absorption of the normal butenes is low, the product should be almost entirely free from compounds derived from the *n*-butenes. Even so, it is possible to identify traces of such compounds in crude di-isobutene, e.g. 3,4,4-trimethylpentene and di-*sec*-butyl ether, the latter being readily recognizable by its characteristic odour.

The hydration of isobutene to tertiary butyl alcohol can be effected by relatively weak acid, but experiments carried out at 0° C. with a solution of isobutene in gasoline showed that while with 50% acid absorption is reasonably rapid, concentrations between 55 and 65% are best suited to technical operation. Since with 65% acid, particularly at temperatures in the neighbourhood of 38° C., polymerization becomes appreciable, there is a tendency for di-isobutene to be formed and carried away in the effluent hydrocarbon layer. Another factor of considerable importance in determining the optimum concentration of acid for absorption of isobutene is the effect of acid concentration on the proportions of the polymerides formed during polymerization. This effect will receive further consideration at a later stage, but it may be noted here that 65% acid is about the highest concentration which may be employed if a high proportion of the dimeride is desired. Although the trimeride yields on hydrogenation a product—'iso-dodecane'—comparable in the engine with iso-octane, it possesses too high a boiling range (175–80° C.) to meet many aviation gasoline specifications. Taking these considerations into account, acid concentrations between 55 and 65% by weight are generally used, a concentration of 64·5% apparently being favoured in America.

The reaction involving the absorption of isobutene in a dilute sulphuric acid solution and the consequent conversion of a molecule of water into a molecule of tertiary butyl alcohol is accompanied by a very considerable increase in the volume of the acid solution and at the same time the specific gravity of the solution falls rapidly. The relationship between amount of isobutene absorbed per gallon of acid and specific gravity of the resulting alcohol-acid solution is shown in Fig. 2 for three strengths of acid. The course of absorption can readily be followed from the specific gravity of the solution. It should be noted that during absorption of isobutene, although the weight fraction of sulphuric acid steadily diminishes, the mol. fraction remains constant.

As the reaction

$$C_4H_8+H_2O \rightleftharpoons C_4H_{10}O$$

is reversible [24, 1931], certain precautions should be observed to avoid loss of isobutene in the effluent hydrocarbon layer. The factors to be considered are (1) time of contact, (2) acid concentration, (3) alcohol/acid ratio, and (4) temperature.

The time of contact necessary is determined by plant

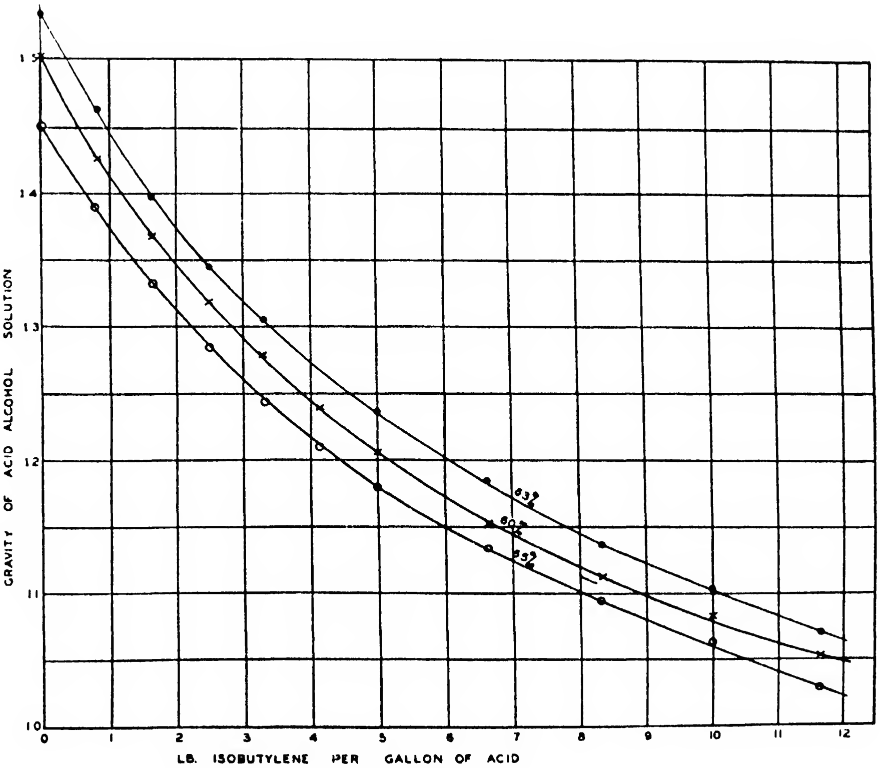


FIG. 2.

considerations but should in all cases be sufficiently long to enable equilibrium to be attained between the hydrocarbon and acid layers. With fresh acid and intimate mixing absorption is at first rapid, but with the accumulation of tertiary butyl alcohol this falls off, at first slowly and later more rapidly. To ensure rapid absorption it is therefore desirable to work to a limiting alcohol content.

Within the range of acid concentrations normally employed in the process there appears to be only slight variation in the equilibrium concentration of isobutene in the hydrocarbon layer.

There is yet another reason for limiting the alcohol concentration. Although in the reaction equilibrium is almost entirely in favour of alcohol, a definite amount of isobutene remains in the hydrocarbon layer. Since this must necessarily increase with increasing alcohol concentration, the higher the latter the greater the isobutene loss. It is therefore more efficient in single-stage extraction to use a large volume of acid and to limit the absorption per cycle to a comparatively low figure. In practice it is convenient to operate to an acid gravity of 1·20–1·30 corresponding with alcohol contents equivalent to 2–6 lb. isobutene per gallon of acid depending on the original acid concentration.

For similar reasons it is advantageous to operate at temperatures as low as possible. Increase in temperature not only favours the equilibrium isobutene content in the hydrocarbon layer but increases materially the absorption of normal butenes. If absorption temperatures are sufficiently high, slow spontaneous polymerization occurs and there is a loss of polymer in the effluent hydrocarbon layer. In practice it has been found that absorption temperatures as high as 32–38° C. may be employed when using 60% acid without excessive absorption of normal butenes and without observable loss of polymer in the effluent hydrocarbon. Since the reaction is strongly exothermic, provision must be made to dissipate the heat liberated, which is quite considerable. Calculations based on Francis and Kleinschmidt's data [11, 1930] gave the value of 470 B.Th.U. per lb. of isobutene dissolved without taking into consideration the heat of solution of alcohol in weak acid. Calculations based on heats of combustion, again neglecting heats of solution, gave the somewhat lower value of 407 B.Th.U. per lb., while others based on Parks' data gave a much lower figure in the neighbourhood of 300 B.Th.U. per lb.

In practice the process is best conducted in a countercurrent continuous system where many of the abovementioned difficulties are largely overcome.

Polymerization.

The acid-alcohol mixture leaving the absorption vessel contains, besides sulphuric acid, water, tertiary butyl alcohol and a small amount of hydrocarbons in solution. It is passed into the polymerizing vessel and heated until polymerization is complete. Since the decomposition of the alcohol must regenerate completely the water consumed in its formation, it follows that when polymerization is complete the concentration of the recovered acid should be identical with that originally fed into the absorption plant. Actually there may be some slight loss of water from the system as there is a tendency for small amounts of tertiary butyl alcohol to be carried away in the product. The course of the polymerization can conveniently be followed by the gravity of the acid layer.

Crude di-isobutene leaving the polymerizer consists essentially of a mixture of di- and tri-isobutene, accompanied by some dissolved isobutene and other hydrocarbons dissolved in the acid-alcohol mixture, small amounts of higher boiling polymers and traces of tertiary butyl alcohol. The amount of isobutene remaining dissolved in the final product is determined by conditions existing in the polymerizer, such as the temperature and pressure at which the reaction is carried out. In practice most of the isobutene regenerated is disengaged and may be taken back to the gas-compression plant. The actual proportions in which the three main products, isobutene, di-isobutene and tri-isobutene, are formed during polymerization are determined by three main factors. Two of these, the acid concentration employed and the acid/alcohol ratio, are associated with the absorption stage. The third, and possibly the most important, is the temperature at which polymerization is effected, a factor completely independent of absorption conditions.

Some mention has already been made of the effect of acid concentration upon the composition of the final products. If a sufficiently low acid concentration is employed the acid-alcohol solution gives an almost entirely theoretical yield of isobutene, a fact upon which is based a convenient method for its preparation. With increasing concentration, however, the formation of isobutene decreases and polymerization occurs until eventually the product consists entirely of polymerides, little or no isobutene being regenerated. This reduction in isobutene formation is not the only effect produced by increase in acid concentration, for there is a simultaneous tendency towards the production of polymers of higher molecular weight at the expense of the lower. Fortunately the acid concentration range which gives rapid and effective isobutene absorption in the first stage of the process coincides with that at which isobutene formation in the polymerizing stage is low and polymer formation high. Even over the range of acid concentration 50–65% there is an appreciable change in the proportion of the polymers formed. Thus, while isobutene regeneration is very marked with 50% acid, it is almost non-existent with 65% acid. On the other hand, trimeride formation, which is comparatively small at the lower concentration, reaches 20–30% at the higher figure. The product normally formed when using 55% acid contains approximately 80% of the dimeride and 20% of the trimeride. Higher polymers are present but are not formed to any considerable extent—about 5%—with acid of 60% concentration. Since the acid/alcohol ratio resembles the acid concentration in that it is generally limited to a comparatively narrow range, it does not require very serious consideration. It is, of course, actually possible to carry the absorption to a stage at which the acid layer consists almost entirely of sulphuric acid and tertiary butyl alcohol. This, as has already been pointed out, is undesirable because isobutene absorption becomes slow and inefficient. It is, moreover, undesirable for another reason, because increase in the alcohol/acid ratio favours isobutene regeneration.

The temperature at which polymerization is effected is probably the most important factor of all since it determines the rate at which the reaction proceeds and also influences to a very marked degree the proportions of the polymerides formed. At higher temperatures polymerization is rapid and the tendency is towards the lower molecular weight products, much isobutene escaping. Lower temperatures require a much longer time for complete reaction and less isobutene is formed. This is particularly well illustrated by the spontaneous polymerization of an acid-alcohol solution (corresponding with 60% acid) over a period of several weeks at room temperature when the upper layer of polymer consisted very largely of the trimeride. The same solution heated to 100° C. for a short time gave a product containing 80% di-isobutene with only 20% of the trimeride. Rough determinations have indicated that a rise of 10° C. more than doubles the rate at which alcohol decomposition and polymerization proceed. Experience has shown that 80° C. is a suitable temperature although as wide a range as 60–90° C. has been successfully employed.

The pressure at which polymerization is effected may also be varied considerably but it is perhaps most advantageous to operate under the pressure prevailing in the absorption stage of the process. Increase of pressure reduces the tendency of regenerated isobutene to escape polymerization. The pressure required to reduce the escape of isobutene to a low figure varies, of course, with the alcohol/acid ratio of the solution entering the polymerizer, but with solutions of specific gravities in the range 1·20–1·30 this pressure need not be in excess of the natural vapour pressure of the hydrocarbon layer in the absorption vessels.

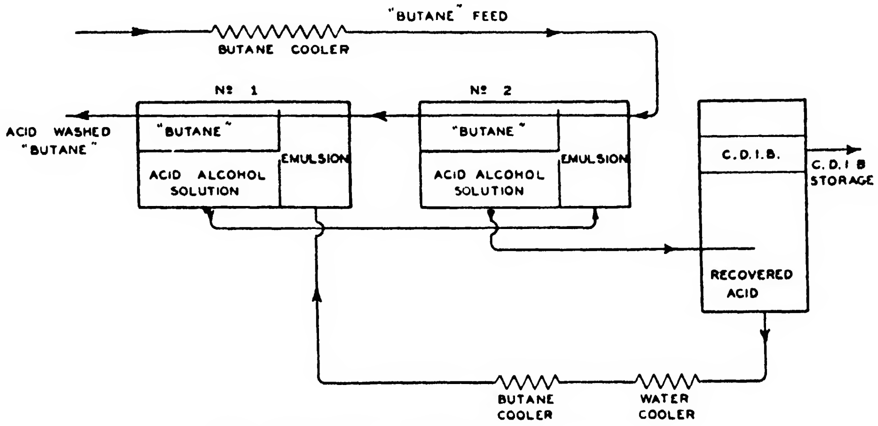


FIG. 3. Flow diagram of isobutene polymerization.

Continuous Operation.

While there are usually distinct advantages to be gained by operating any process continuously, this is especially true of the production of di-isobutene, particularly if a counter-current system of absorption is employed. The desirability of such a system is obvious when the reversibility of the reaction in which isobutene, water, and alcohol are in equilibrium is considered. Extraction efficiencies are necessarily higher since material of low isobutene content is brought into contact with fresh acid while the raw feed stock meets acid already high in alcohol content. With a sufficient time of contact and provision to remove the heat of reaction (thus maintaining temperatures below the point where polymerization becomes noticeable), absorption proceeds satisfactorily. As the operation may without harm be performed up to 32–38° C., it is more convenient to work under pressure than to endeavour to maintain temperature below the boiling-point of the hydrocarbon fraction and dispense with pressure equipment.

Polymerization can be effected continuously by passing the alcohol-acid solution into a vessel provided with steam-heating coils. As the specific gravity of the solution is comparatively low, the feed line is most conveniently placed at a point slightly below the interface of the crude di-isobutene and acid layers. Here it is decomposed to yield polymer which rises to the surface and a more dense solution which tends to sink to the bottom of the vessel. Polymerization proceeds steadily and fully recovered acid is obtained at the bottom. Crude di-isobutene and recovered acid can thus be drawn off continuously at different levels. The crude di-isobutene, in rising through the alcohol-acid solution, tends to carry with it some dissolved alcohol, especially near the surface where the alcohol/acid ratio is highest owing to the low specific gravity of the solution entering the polymerizer. The alcohol content of the crude di-isobutene may be as much as 1%—varying with the depth below the interface of the feed line and the alcohol/acid ratio of the feed—and it is obvious that water, in the form of tertiary butyl alcohol, is continuously withdrawn from the system. This loss should be corrected by the continuous addition of the equivalent amount of water.

As the acid at concentrations employed in the process is highly corrosive towards steel, it is necessary to protect the plant against corrosion. This is most conveniently done by lead-lining of the equipment.

Product.

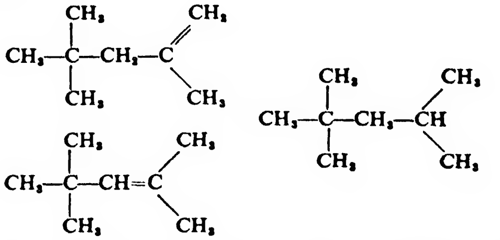
The crude product leaving the polymerizer is generally pale yellow in colour and is given a neutralizing wash with soda or lime before distillation. Since it consists almost entirely of di- and tri-isobutenes with some dissolved gas, no very rigorous fractionation is necessary to produce almost pure di-isobutene. Any gas present is passed back to the compression plant for recycling while the tri-isobutene is collected as a separate distillate. The di-isobutene cut is a water-white product generally possessing a somewhat sweetish odour owing to the presence of traces of oxygen compounds—probably mainly di-*sec*-butyl ether derived from absorbed *n*-butenes. Although it is known to possess excellent blending properties, especially in lower concentrations, there are no published data fully describing its use or behaviour in the engine.

Iso-octane

Parks and Todd [23, 1936] concluded from a thermodynamic study of the energy changes involved that the direct addition of isobutene to isobutane to form iso-octane was theoretically possible, but their inference from the small free energy change was that the reaction would be exceedingly difficult to perform. Consequently they did not publish their data until it was actually shown by Ipatieff and v. Grosse [15, 1935] that the direct addition of paraffins to olefines, in the presence of boron fluoride and nickel powder and water, was experimentally possible. Such reactions, however, need considerable development, and it will probably be some time before they are commercially operated.

The preparation of iso-octane by the hydrogenation of di-isobutene using a nickel catalyst was first described by Edgar [9, 1927], who suggested its use as a standard reference fuel for anti-knock measurement.

It is obvious from an examination of the formulae of the two isomers present in di-isobutene that both on hydrogenation must give one individual paraffin, 2,2,4-trimethylpentane:



Iso-octane prepared in this way has a pleasant odour and after careful purification gives the following constants:

Boiling-point	99·37° C.
Freezing-point	−167·6° C.
Specific gravity 20°*C*/4°*C*	0·6920
Refractive index 20°*C*/*D*	1·3915

Commercial iso-octane is to-day produced by the hydrogenation of di-isobutene, an operation which can readily be effected in the laboratory with the aid of a number of catalysts. The reaction, which is exothermic, has been examined by Crawford and Parks [6, 1936] who found experimentally for the reaction

$$C_8H_{16}\,(\text{liq.}) + H_2 \rightarrow C_8H_{18}\,(\text{liq.}) \qquad \Delta H_{298} = -28{,}580 \text{ cal.}$$

as against a deduced value of

$$\Delta H_{298} = -28{,}100 \text{ cal. } (\pm 3{,}000 \text{ cal.}).$$

While no published information concerning large-scale operation is at present available, there is little doubt that most of the iso-octane on the market has been produced by hydrogenation using a nickel catalyst (December 1936).

The use of nickel as a catalyst is open to several serious disadvantages, the chief of which is its sensitivity to poisoning, particularly by sulphur derivatives or carbon monoxide. Since the latter is to a greater or less extent a common constituent of hydrogen derived from steam reactions, it is necessary either to employ very elaborate purification processes or, better, to use electrolytic hydrogen—an expensive material economically possible only where electrical power is extremely cheap.

While the presence of sulphur in the di-isobutene can to a large extent be limited either by the use of gases derived from non-sulphurous cracking stocks or by the removal of the sulphur bodies present in the C_4-cut, it is difficult to reduce the final sulphur content to the low figure necessary for nickel catalysts. No exact value is available for the limiting sulphur content, but it is probably of the order of 0·01%. Naturally hydrogenation can be effected over nickel with a very much higher sulphur figure than this, but the life of the catalyst is considerably reduced. For satisfactory catalyst life an even lower figure is desirable, and this is extremely difficult to attain. Therefore, unless there is available a satisfactory method of catalyst regeneration, high catalyst costs are entailed even though the spent catalyst may have a definite scrap value on account of its nickel content.

Nickel catalysts lend themselves for use either in vapour-phase or liquid-phase processes. While vapour-phase operation employs a supported nickel catalyst on an inert carrier—which may be nickel itself—it is difficult to control successfully on a large scale owing to the exothermic nature of the reaction. Not only is it difficult to dissipate the heat formed—a common source of trouble with catalysts of this type—but at the actual catalytic surface such high temperatures are reached that depolymerization and other reactions take place to some extent. Operation under pressure increases the rate of hydrogenation.

Liquid-phase hydrogenation follows the procedure normally adopted in fat-hardening. The catalyst usually employed, an easily decomposed nickel compound either alone or supported on an inert carrier such as diatomaceous earth, after previous reduction in hydrogen is added to di-isobutene in a pressure vessel provided with means for circulating hydrogen and maintaining the catalyst in suspension. The operation is conducted at approximately 160–200° C., when hydrogen is rapidly absorbed and iso-octane produced. Although essentially a batch process, it is possible by suitable modification to make the process continuous, the catalyst being retained in the plant. Liquid-phase operation holds an advantage in that, as the catalyst is surrounded with liquid, heat is more easily dissipated and high local temperatures avoided.

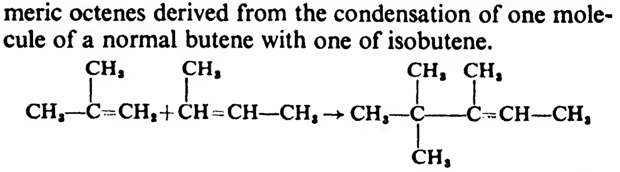
Catalytic activity eventually falls off due to poisoning, analyses of the spent catalyst generally show a small sulphur content, probably present as γ-nickel sulphide.

Several catalyst regeneration processes have been described varying from electrolytic oxidation to treatment with weak volatile organic acids such as acetic acid, followed by reduction, but other than the electrolytic oxidation process [25] these do not appear very successful.

A small amount of water is generally obtained during hydrogenation. Whether this is due to oxide remaining in the catalyst or to traces of oxygen compounds in the di-isobutene is uncertain. Its formation is unimportant and does not affect the process as far as is known. The progress of the hydrogenation is conveniently followed by the bromine or, better, the iodine value of the product. Specific gravity determinations alone do not give a safe indication since owing to depolymerization—particularly with a new and active catalyst—a misleadingly low figure is obtained owing to the presence of isobutane formed from isobutene by hydrogenation.

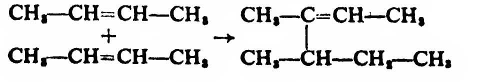
Selective Polymerization.

The recent discovery by the Universal Oil Products Company that 100 octane fuel can be produced by hydrogenation of the condensation product from *n*-butenes and isobutene is extremely important, as this material will probably largely displace iso-octane in the future. If instead of the wide fraction containing ethylene, propylene and the butenes employed in the normal catalytic (phosphoric acid) polymerization process a narrow cut containing only the C_4 hydrocarbons is employed, there is obtained a high yield of octenes, boiling somewhat higher than di-isobutene, in the range 100–20° C. This material consists largely of isomeric octenes derived from the condensation of one molecule of a normal butene with one of isobutene.



$$CH_3-\overset{CH_3}{\overset{|}{C}}=CH_2+\overset{CH_3}{\overset{|}{C}H}=CH-CH_3 \rightarrow CH_3-\underset{\underset{CH_3}{|}}{\overset{CH_3}{\overset{|}{C}}}-\overset{CH_3}{\overset{|}{C}}=CH-CH_3$$

The main product is apparently 3,4,4-trimethyl pentene boiling at 110° C. It is almost certainly accompanied by 2,3,4-trimethyl pentene-2 formed by molecular rearrangement [31, 1936], di-isobutene in greater or less amount depending upon the relative proportions of the butenes present in the starting material, and some 3,4-dimethylhexene derived from normal butenes.



$$\begin{array}{c}CH_3-CH=CH-CH_3\\+\\CH_3-CH=CH-CH_3\end{array}\rightarrow\begin{array}{l}CH_3-C=CH-CH_3\\\qquad\ \ |\\CH_3-CH-CH_2-CH_3\end{array}$$

Higher boiling constituents corresponding with trimerides are also produced, but since they are not suitable for inclusion in aviation gasoline need not be considered here. The process is of particular interest as one molecule of octene is formed from one of isobutene instead of from two as with di-isobutene, so that the yield of useful product is approximately doubled for a given quantity of isobutene. As there is always an excess of normal butenes over isobutenes in cracker gases this is of considerable importance, particularly as the product on hydrogenation gives a fully saturated paraffinic fuel of 96 octane number and good lead response comparable in all respects with iso-octane. It consists largely of 2,2,3-trimethylpentane, b.p. 110·5–110·8° C., d_{15}^{15} 0·7219, and n_D^{25} 1·4164 [5, 1912].

Whitmore and Laughlin [32, 1933] consider that this material contained olefines and that the correct constants for pure 2,2,3-trimethylpentane are: boiling-point (Cottrell) 110·2° C., n_D^{20} 1·4030, d_4^{20} 0·7173.

REFERENCES

1. Bataffsche Petroleum Maatschappij. B.P. 358,068 (1931).
2. Butlerov, A. *Ann.* **180**, 247 (1876); ibid. **189**, 48 (1877); *Ber.* **12**, 1482 (1879).
3. Butlerov, A., and Gorianov. *Ann.*, **169**, 147 (1873).
4. Campbell, J. M., Lovell, W. G., and Boyd, T. A. *Ind. Eng. Chem.* **23**, 555 (1931).
5. Clarke, L., and Jones, W. N. *J.A.C.S.* **34**, 173 (1912).
6. Crawford, B. L., and Parks, G. S. *J.A.C.S.* **58**, 373 (1936).
7. Davis, H. S. *J.A.C.S.* **50**, 2781 (1928).
8. Dobryanski, A. *Neft. Khoz.* **9**, 565 (1925).
9. Edgar, G. *Ind. Eng. Chem.* **19**, 145 (1927).
10. Egloff, G. Polymer Gasoline. A.C.S. Meeting (Petroleum Division), April 1936.
11. Francis and Kleinschmidt. *A.P.I. Bull.* **3**, 93 (1930).
12. Hurd, C. D., and Spence, L. U. *J.A.C.S.* **51**, 3561 (1929).
13. I.G. Farbenindustrie. B.P. 448,690.
14. Ipatieff, V. N. *Ind. Eng. Chem.* **27**, 1071 (1935).
15. Ipatieff, V. N., and v. Grosse. *J.A.C.S.* **57**, 1616 (1935).
16. Kline, G. M., and Drake, N. L. *Bur. Stand. J. Res.* **13**, 709 (1934).
17. Kondakov, I. *J. Russ. Phys. Chem.* **24**, 309 (1893); *J. pr. Chem.* (2), **54**, 442, 454 (1896).
18. Lebedev, A. N., and Filonenko, E. P. *Ber.* **58**, 163 (1925).
19. Lebedev, A. N., and Koblianski, G. G. *Ber.* **63**, 1432 (1930).
20. McCubbins, R. J., and Adkins, H. *J.A.C.S.* **52**, 2547 (1930).
21. Michael, A., and Brunel, R. F. *Amer. Chem. J.* **41**, 118 (1909).
22. Otto. *Brenn.-Chem.* **8**, 321 (1927).
23. Parks, G. S., and Todd, S. S. *Ind. Eng. Chem.* **28**, 418 (1936).
24. Rice, F. O. *J.A.C.S.* **53**, 1959 (1931).
25. Technical Research Works and Lush. B.P. 203,218.
26. Tongberg, C. O., Pickens, J. D., Fenske, M. R., and Whitmore, F. C. *J.A.C.S.* **54**, 3706 (1932).
27. Weizmann, C., and Legg, D. A. *J.S.C.I.* **40**, 675 A (1921).
28. Whitmore, F. C., *Ind. Eng. Chem.* **26**, 94 (1934).
29. Whitmore, F. C., and Church, J. M. *J.A.C.S.* **54**, 3710 (1932).
30. Whitmore, F. C., and Wrenn, S. N. *J.A.C.S.* **53**, 3136 (1931).
31. Whitmore, F. C., Laughlin, K. C., Matuzzishi, Crooks, and Fleming. A.C.S. Meeting (Pittsburg), Sept. 1936.
32. Whitmore, F. C., and Laughlin, K. C. *J.A.C.S.* **55**, 2067 (1933).
33. Van Winkle, R. *J. Amer. Pharm. Assoc.* **17**, 544 (1928).

WHITE OILS

By F. M. ARCHIBALD, M.A., Ph.D.
Plant Chemist, Standard Oil Company of New Jersey

WHITE oil, also known as medicinal oil or petrolatum liquidum to the pharmacist, is highly refined mineral oil. It is colourless, tasteless, and almost non-reactive to strong chemical reagents. Its original use for medicinal purposes now affords a minor outlet. White oils are used in diverse fields such as in textile work, in horticultural sprays, in cosmetics, for lubricating enclosed machines, &c.

The first 'white oil' was a straw-coloured crude oil produced in the Surakhany district of Russia. For a century or more it was in great demand because of its reputed therapeutic properties. This established market for medicinal oil accounts for the fact that refined white oil was first made in Russia. In 1913 'Russian oil' became introduced abroad for the treatment of chronic constipation. The interesting properties of the material, as well as the price that it commanded, soon stimulated the invention of new uses for it and new processes for its manufacture.

White oil is commonly made to-day by the action of fuming sulphuric acid on petroleum distillates with the necessary subsequent washing and filtration through adsorbent clay.

Petrolatum liquidum is the highest grade of white oil. Its quality is measured chiefly by its resistance to hot concentrated sulphuric acid. This test is described below.

Petrolatum liquidum must be colourless and free from objectional taste or odour. The specific gravity specified in the *U.S. Pharmacopoeia, 1926*, is 0·828 to 0·905 at 25° C. and the kinematic viscosity from 0·370 to 0·381 at 37·8° C. [5]. It is used as a vehicle or solvent for drugs in sprays, dressings, and tonics for internal and external use. Although white oil is harmless taken internally, its use in foods is prohibited by pure food laws in most countries. It is, however, occasionally used as fat substitute in reducing diets, for example, in salad dressing.

White oils in a wide range of viscosity from that of kerosine to that of medium-heavy lubricating oils are made for special purposes, and the degree of refining is frequently modified where the so-called technical white oils may be used. It is therefore possible to define white oils somewhat broadly. In specific cases a chemical test is used to specify the quality of the oil. For example, oil heated with stannic chloride yields a sludge if olefinic material is present. Oils for horticultural sprays are sometimes tested for sulphonatable matter in a quantitative method using sulphuric acid, as described by Gray and de Ong [1, 1926]. In certain cases resistance to oxidation has been used in testing white oils. The pharmacopoeia hot-acid test has been modified to give a quantitative indication which is used in evaluating the lower grade white oils. This is discussed below. The colour specification varies from 15 to 30+ Saybolt scale and viscosity from 35 to 350 sec. at 100° C. Saybolt.

In the production of white oil the lubricating property of the stock is not destroyed, but it is distinctly modified by changes in its ability to wet certain metals. When desired, this may be corrected by the addition of traces of fatty acid, soap, or other material. The oxidation characteristics of the oil is also modified by the refining process. Ordinary lubricating oil starts to oxidize immediately in an atmosphere containing oxygen, and the absorption of the oxygen proceeds at a constant rate. White oil, on the other hand, does not absorb oxygen for a time. This inhibition period depends on the temperature. Eventually reaction takes place and proceeds autocatalytically at an increasing rate. This phenomenon, studied by Haslam and Frolich [3, 1927], is similar to the behaviour of motor-fuel, and may be corrected in a similar way by adding as inhibitors aromatic amines, phenols which lengthen the inhibition period.

Manufacture

In the manufacture of white oil there are the following considerations:

1. The selection of a suitable distillate from a suitable crude oil so that the finished oil will have the desired properties.
2. The acid treatment of the distillate in the most economical manner.
3. The final purification by solvents and adsorbents.
4. Inspection.

1. Chemically, the white oils are naphthenes or cycloparaffins with traces of paraffins. White oil made from different crudes, however, vary widely in the relation between the specific gravity and viscosity. It happens that the original Russian oils had a high specific gravity compared with that of most white oils of the same viscosity from other sources. This has prejudiced many white oil consumers in favour of high specific gravity. In Europe white-oil stocks are manufactured, not only from Russian crude, but from imported crudes of naphthenic type. In America, Peruvian stocks were popular for a time because of the high specific gravity white oil obtained. The semi-asphaltic crudes of Texas also give white oils of the same viscosity-gravity relationship as that of the Russian oils. In order to maintain uniform quality with a given crude stock, it is necessary to select a uniform cut by fractional distillation.

2. Fuming sulphuric acid is universally used in white oil manufacture since it is both cheap and efficient and affords the most direct method of meeting the hot-acid test specifications. As preliminary steps in the refining 66 Bé. acid or aluminum chloride may be used, or extractive agents such as phenol or sulphur dioxide. Such procedure, however, does not increase the overall white-oil yield or change the properties of the product. The acid-treating technique does not differ from the procedure used in general acid treating. The requirements are: good dispersion of acid in the oil, temperature control, and the application of the acid in several dumps with the removal of the sludge between dumps. As much as 50% by volume of 20% oleum may be required to make pharmaceutical oil.

3. The accumulation of sulphonates in the oil tends to slow down the action of the acid towards the end of the treating. In some cases it is necessary to interrupt the treating and remove them. In all cases the sulphonates are removed at the end of the treating by one of the following methods:

a. The acid oil may be neutralized with caustic soda and washed with a small volume of hot water. This procedure avoids emulsions if the wash contains excess-alkali.

b. The neutralized acid oil may be distilled overhead with fire and steam with care to avoid cracking. The alkali sulphonates remain in the still bottom.

c. The sulphonates may be removed by means of water soluble inorganic solvents, such as alcohol or acetone.

The use of solvents is in general favour since the realization of the useful properties of the sulphonates. Although it makes necessary special equipment for the recovery of the solvent, this method is generally the most economical. After the removal of the residual solvent from the extracted oil, it is treated with clay to produce the finished white oil.

Floridin is in general use in America for finishing white oils. Activated clays are somewhat less effective in removing the traces of colour and taste. For percolation filters, 30- to 60-mesh per in. screened clay is used. Finer clay is used for contact filtration. Filtration temperatures above 150° F. are undesirable because of the susceptibility of the oil to oxidation. Dilution of the oil before filtration is impracticable due to the difficulty of removing the solvent without harming the finished oil. The used clay may be reclaimed and re-used to a limited extent. The consumption of floridin is sometimes as high as 200 lb. per barrel of oil produced. This depends on the stock and on how well the treating has been carried out.

The manufacture of white oil differs from lubricating oil processes mainly in the degree of thoroughness in which the steps are carried out. The chemical theory involved is necessarily vague since the chemical nature of the oils themselves is imperfectly understood. The white oil treating is interesting where it goes beyond ordinary acid treatment; that is to say, after the first portion of acid. In the later acid portions the sludge appears to be a mixture of fairly definite compounds in the unused acid. The by-products of white oil treating are discussed under 'Sulpho Acids' (p. 2840). As stated above, the accumulation of sulphonates in the oil inhibits the action of the acid towards the end of the treating. This is because the acid acts partly upon the sulphonates, converting them to tar. The polymers produced by the oleum in the first acid portions disappear on further acid treatment.

The sludge from white oil acid treating contains 50% or more of free sulphuric acid. On standing it forms a solid residue similar to acid cake and liberates a quantity of dark-coloured oil-soluble material. For this reason the sludge is promptly removed after each addition as in lubricating oil treating practice.

Finished white oil intended for medicinal purposes is protected from contamination since it readily dissolves odours. Exposure to sunlight hastens oxidation. In a week or so a distinctly rancid taste develops. On further exposure the oil may even become yellow. Technical white oils generally require less care, although their sensitivity to light may be greater.

4. In the general inspection the regular lubricating oil physical tests are used. A sodium plumbite test for sulphur is mentioned in the *British Pharmacopoeia*, but invariably an oil passing the hot-acid test passes most other chemical tests as well.

Hot-Acid Test

In making the hot-acid test it is essential to use sulphuric acid of a standard strength, say 95% sulphuric acid plus or minus 0·2%. Equal volumes of the acid and the oil are placed in a dry, clean, glass-stoppered test-tube and immersed in boiling water for 10 min. At 30-sec. intervals the tube is shaken briskly and returned to the water-bath. After finally cooling and settling, the oil layer should be colourless and the acid layer not darker than pale amber. This colour has been tentatively defined by the U.S. Customs Department by the use of a dye [4, 1932]. A methyl-orange solution in water (0·0008% concentration) has been suggested. For measuring lower acid tests on technical oils a scale of colour based on inorganic solutions has been used by Weiss [6, 1918]. A colorimeter, using standard colour glasses as described below, is both convenient and accurate. The reproducibility of hot-acid colours depends on adherence to a standard technique of shaking. A complete discussion of the hot-acid test has recently been given by Hampshire and Page [2, 1934].

The stability of white oil to oxidation is readily measured by placing a sample in a steam-bath at 100° C. overnight. A stable oil will have a hot-acid test unchanged and will not have developed a rancid taste. As a test for white-oil stability, 16 hr. at 100° C. has been found to be equal to more than 2 years storage at room temperatures.

Typical White Oil Inspections

Sample	*Sp. Gr. 60° F.*	*Say. Vis. 100° F. sec.*	*Pensky flash*	*Cloud °F.*	*Pour °F.*	*Hot-acid test*
A	0·890	350	375	38	−30	300
B	0·886	225	365	52	−30	250
C	0·846	82	360	50	+10	230
D	0·827	50	310	48	+35	60

Note: This hot-acid colour scale is ten times the millimetres depth of acid required to match a N.P.A. colour disk no. 2½. The Lovibond analysis of the disk is 27Y 4·6R. A reading of 200 corresponds approximately to U.S. P. pale amber colour.

Miscellaneous Properties of White Oils

Sulphur determination (bomb method)	0·05–0·1%
Surface tension (drop weighed method)	45–55 dynes per cm.
Refractive index at 26° C.	1·46–1·48
Iodine number (Hanus method)	9·2–0·8
Vapour pressure 125 Vis. WO	110° C. 0·005 mm. Hg.
,, ,, ,,	134·5° C. 1·0 ,,
,, ,, ,,	167·5° C. 3·0 ,,
,, ,, ,,	183·2° C. 6·0 ,,
,, ,, 340 Vis. WO	184° C. 9·0 ,,
Latent heat of evaporation	50 calories per gramme
Distillation atmospheric pressure	Initial, 570–670° F. Final, 680–750° F.

Viscosity temperature index is slightly less than that of the better grades of Pennsylvania lubricating oil. For example, a low cold test oil of 85 sec. viscosity Saybolt at 100° F. was 2,000 sec. at 0° F.

Stability of White oils

Exposure to sunlight at room temperature:
- Medium quality of oil is off colour in 7 days.
- Good quality of oil is off colour in 6 weeks.

Exposure to air at 100° C.:
- Poor quality oil very rancid in 4 hr.
- Medium quality oil slightly rancid in 8 hr.
- Good quality oil not rancid in 16 hr.

The oxidation of white oil is catalysed by copper.

REFERENCES

1. Gray, G. P., and de Ong, E. R. *Ind. Eng. Chem.* **18,** 175 (1926).
2. Hampshire, C. H., and Page, G. R. *Quart. J. Pharm. and Pharmacol.* **7,** 354 (1934).
3. Haslam, R. T., and Frolich, P. K. *Ind. Eng. Chem.* **19,** 293 (1927).
4. *Oil, Paint and Drug Reporter*, **47,** 29 Aug. (1932).
5. *United States Pharmacopoeia, 1926*, pp. 281; *British Pharmacopoeia, 1914*, pp. 283.
6. Weiss, J. M. *Ind. Eng. Chem.* **10,** 1006 (1918).

SULPHO ACIDS

By F. M. ARCHIBALD, M.A., Ph.D.

Plant Chemist, Standard Oil Company of New Jersey

SULPHO acids are the product of the reaction of sulphuric acid with petroleum. The term broadly includes acid products found in the acid sludge and acid products in the treated oil. They are known respectively as green acids and mahogany acids because of their colour in the crude state. They are used in both the neutral and acid state as emulsifying, demulsifying, or dispersion agents in a large variety of applications. The ordinary acid treatment of oil does not produce sulpho acids of good quality since only sufficient acid is used to remove the lower-grade impurities, such as asphaltenes and sulphur compounds. The best raw material is obtained by the later additions of acid when treating white oil.

The mahogany acids or oil-soluble sulphonic acids are extracted from the treated oil with alcohol and generally after several treatments with acid. The acids are neutralized with alkali since they are most commonly used as the alkali soaps.

Further purification from mineral salts, &c., is made by dissolving the soap in a dry organic solvent and settling or filtering. The action of a mild oxidant such as hydrogen peroxide is sometimes used to improve the colour. Ordinarily the soap contains up to 10% of oil. This may be removed from a dilute alcoholic solution of the soap by repeated extraction with petroleum ether. The dried soap is then a resinous solid, yellow to orange in colour, hygroscopic, softening below 60° C.

The sulphonic acid and its alkali soaps can easily be dispersed in water in all proportions. The alkali soaps are soluble in oil but not the heavy metal soaps. Sodium sulphonate is stable to heat at 130° C. but at 200° C. breaks down rapidly to a tarry material. Solutions of the sodium sulphonate in oil make it emulsifiable in water in all proportions. From 5 to 30% soap is required depending on the oil and on the purity of the soap. The quality of the emulsion is frequently improved by adding to the oil traces of sodium resinates or triethanolamine oleate.

A crude form of mahogany soap made from low viscosity oils is used for splitting fats. The principal use of mahogany soap is in textile oils, metal-cutting oils, and in miscellaneous oil emulsions. Numerous patented uses for mahogany soaps are given by Carleton Ellis [1, 1934].

The mahogany acid from a given oil is a fairly definite chemical compound. The combining weight is the same as the molecular weight, since the acid is monobasic and may range from 350 to 500-g. equivalents, depending on the viscosity of the oil from which it is made. The mahogany acids are strong acids as shown by the fact that the alkali soaps are not hydrolysed in water. The amount of mahogany soap in oil may be estimated by extraction with 50% aqueous alcohol and washing back with petroleum ether. If the combining weight of the soap is known, the soap may be estimated from its ash which contains just one-half of the sulphur trioxide content of the soap and is weighed as sodium sulphate.

The sodium sulphonate may be converted to mahogany acid by washing it in an ether solution repeatedly with strong hydrochloric acid. In this way the soda may be removed, the acid may be dried, and its combining weight determined directly. Schestakoff [2, 1913] gives as the empirical formula $C_nH_{2n-12}SO_3$.

The green acids are separated from acid sludge by diluting the sludge with water sufficient to cause the free sulphuric acid to separate as a 50% solution. Sulphuric acid of that strength has a minimum solubility for the green acids. Temperatures up to 100° C. do not seriously affect the quality of the green acids after dilution. For many purposes the green acids are used without further purification. On adding further water they go completely into solution and may be neutralized with ammonia or caustic alkali, giving a brown soap soluble in water in all proportions, but containing colloidal material which separates on standing.

Unlike the mahogany acids, the green acids are definitely a mixture. They contain individuals of molecular weight ranging from 150 to 1,000. In further purification advantage is taken of the fact that the heavier acids form insoluble calcium soaps, whereas the light acids give calcium soaps soluble in water. This precipitation must be made in dilute solutions because the precipitate is bulky and tends to occlude most of the light soaps.

The green sulpho soaps are used in emulsifiers, wetting agents, pickling inhibitors, foaming agents, and dust-laying compounds. Twitchell's reagent used for splitting fats is made from green acids by partial purification, but has largely been superseded by the crude form of mahogany soap mentioned above. Miscellaneous patented uses of green acids are given by Carleton Ellis [1, 1934].

The light green acids were studied by Spiegel in 1891 and termed thumenol-sulphonic acids. He believed the heavy acids to be sulphones [3]. Von Pilat and Sereda (1928) classified the sulpho acids according to the solubility of their calcium salts in ether and in water as alpha, beta, and gamma [4, 1933]. The classification of the green acids by the use of precipitants and solvents in any case is somewhat arbitrary. The amount of soap precipitated by metal salts is proportional to the molecular weight of the metal used. The ammonium soaps are almost completely water soluble.

The green acids are precipitated from dilute acid solutions by fresh albumen or by ethyl benzylaniline. This fact is useful in sludge analysis since the separation is quantitative. The heavy soaps of alkali metals may be extracted from an aqueous solution with benzol. It is difficult to remove from them any associated non-acidic matter. They have not only a lower acidity than the light acids but a higher unsaturation. The empirical formula of the green acids ordinarily varies from $C_nH_{2n-6}SO_4$ to $C_nH_{2n-9}SO_4$.

Spiegel [3, 1891] gives an empirical formula corresponding to $C_nH_{2n-15}SO_4$, which indicates that his sludge was not made by carefully controlled acid treating.

REFERENCES

1. ELLIS, C. *The Chemistry of Petroleum Derivatives,* 1013–30 (Chem. Catalogue Company, New York, 1934).
2. SCHESTAKOFF, P. *J. Russ. Phys. Chem. Soc.* 664 (1913).
3. SPIEGEL, L. *Chem. Ztg.* 772 (1891).
4. VON PILAT, S., and SEREDA, J. *Petr. Z.* 29 (3), 1 (1933).

ICHTHYOL

By G. H. SMITH, Ph.D., A.R.T.C., A.I.C.
Scottish Oils, Ltd.

COMMERCIAL ichthyol is the ammonium salt of the so-called ichthyol sulphonic acids, prepared by sulphonating the crude oil distilled from certain sulphurous shales, and is used principally for its therapeutic effects in skin diseases.

It is recorded that as far back as the sixteenth century the Tyrolese peasants produced, by distilling the local shale, a tarry oil which they found very beneficial in treating wounds, skin diseases, and sores of all kinds. The development of the ichthyol industry, however, really commenced in 1891, when the Ichthyol Geschellschaft-Cordes Hermanni & Co. formed in Hamburg started operations. These shale deposits of the Austrian Tyrol together with similar deposits in Germany, Switzerland, and Italy should be regarded as a special type of shale, since these beds, found in very thin layers, are very rich in fossil fish remains (from which the name ichthyol is derived) and are of value only for the ichthyol that is produced therefrom. Originally the name ichthyol referred to the crude oil, but since the sulphur content was increased by sulphonation, the term ichthyol has applied to the improved product and now denotes the ammonium salt of the ichthyol sulphonic acids.

The first deposits to be worked were those at Seefeld, near Innsbruck on the south slope of the Karwendal mountains which form the boundary between Austria and Bavaria. The yield of oil was 9 to 10% and the sulphur content of oil 3 to 6%. Similar deposits on the German side of the mountains along the valley of the Isar were exploited in 1920, but here, according to Alderson [1, 1923], the shales are exceedingly rich in fossil fish remains and gave 30% of oil. Deposits of the same type of ichthyol shale have been mined and processed near Lake Lugano in Switzerland, yielding an oil termed 'Saurol' which closely resembles ichthyol in its therapeutic properties; the purified oil contains 6 to 7% of sulphur in organic combination Neran [11, 1917]. The Italian deposits which occur in several districts are said to be connected with those of Switzerland.

Analyses of two samples of Ichthyol Shales

	Karwendal oil shale Berl and Schmid [5, 1926]	*Swiss oil shale Alderson* [1, 1923]
Moisture	1·25	2·0
Ash	52·08	47
Total vol. matter	37·98	. .
Nitrogen	0·36	. .
Sulphur	3·98	. .
Oil yield	18% (temp. 545° C.) (press. 10/50 mm.)	21%
Sulphur in oil	about 11%	5·83%

Briefly the process of ichthyol manufacture is as follows: The shale is distilled in iron retorts, which may be stationary or rotary, either under atmospheric or reduced pressure. The oil vapours evolved are condensed, the oil separated from the water and treated with concentrated or fuming sulphuric acid. When all reaction has ceased, sufficient water is added to dissolve the products of sulphonation, which are then salted out with sodium chloride and neutralized with ammonia. This ammonium salt of ichthyol sulphonic acid is known commercially as 'Ichthyol'. Helmers [6, 1894] recovered the ichthyol sulphonic acids from the mixture by neutralizing them with alkalis and separating with solvents such as alcohol, benzene, and chloroform.

Ammonium ichthyol sulphonate is a dense reddish-brown oil soluble in water and also in a mixture of alcohol and ether.

Scheibler [14, 1915] in his classical work isolated and identified a number of thiophene homologues from crude Ichthyol oils. Bauman and Schotten [3, 1912] attributed the formula $C_{28}H_{26}S\ (SO_2OH)_2$ to ichthyol sulphonic acid, and it has been stated that the ammonium salt of this acid is principally $C_{28}H_{26}S\ (SO_2ONH_4)_2$, but the origin of this material, its method of preparation, and indeed its properties must lead to the conclusion that it is a mixture of many compounds. This is demonstrated by Passmore [12,1909] and by Beckurts and Frerichs [4, 1912], who examined samples of commercial ichthyol and their derivatives and substitutes. The latter gives analyses of seven samples of ichthyol, and their constituents varied as shown below:

Dry residue	53·99 to 56·84%	Sulphur as sulphide	6·63 to 7·1%
Total sulphur	10·74 „ 11·27%	Total ammonia	2·95 „ 3·02%
Sulphate sulphur	1·45 „ 1·51%	Amm. sulphate	5·98 „ 6·1%
Sulphonic sulphur	2·54 „ 2·76%	Ash	0·05 „ 0·07%

Oxidation of the ichthyol sulphonic acids by oxidizing agents such as hydrogen peroxide has been applied to render them tasteless and odourless (Helmers [7, 1897]), but this treatment partly destroys its medicinal properties. Knoll & Co. [10, 1897] patented a process whereby ichthyol sulphonic acid is deodorized by treatment with steam under reduced pressure.

Many derivatives and substitutes for ichthyol have been produced, all having more or less the same therapeutic properties; a few of these are given below:

Ichthaldin. Complex compounds of ichthyol sulphur acids and albumin. Helmers [9, 1900].

Ichthyoform. Compounds of ichthyol sulphonic acid and formaldehyde. Helmers [8, 1899].

Thalassol. Produced by sulphonating the crude ichthyol oil by chlor-sulphonic acid and neutralizing the product with ammonia. Schauffer and Faber [13, 1920].

At various times attempts have been made to introduce sulphur artificially into hydrocarbons by heating them with sulphur, but the formation of thiophene derivatives from petroleum oils by this means is only one of many types of reactions that may occur, and consequently the yield is low. Oils thus prepared have been processed similarly to ichthyol crude oil, but the final product is definitely inferior to the real ichthyol (Anon. [2, 1930]).

REFERENCES

1. **Alderson**, V. *Petr. Times*, **9**, 716 (1923).
2. **Anon.** *Petr. Eng.* Feb. pp. 41–4 (1930).
3. **Bauman** and **Schotten**. See Thorpe's *Dictionary of Applied Chemistry*. Longmans Green & Co., New York, **3**, 92 (1912).
4. **Beckurts**, H., and **Frerichs**, H. *Arch. Pharm.* **250**, 478–93 (1912).
5. **Berl**, E., and **Schmid**, W. *Bren.-Chem.* **7**, 49 (1926).
6. **Helmers**. G.P. 82,075 (1893), B.P. 6,044 (1893), U.S.P. 525,784 (11 Sept., 1894).
7. **Helmers**. G.P. 99,763 (1897), G.P. 114,394 (1899), G.P. 120,014 and 120,015 (1899), G.P. 127,505 (1901).
8. —— B.P. 9,157 (1899).
9. —— U.S.P. 649,305 (May 1900), B.P. 14,388 (1899).
10. **Knoll** & Co. G.P. 100,707 (1897), G.P. 118,452 (1899), G.P. 124,144 (1899).
11. **Neran**, L. *Pharm. J.* **98**, 43 (1916).
12. **Passmore**, F. W. *Chem. and Drug.* **75**, 935 (1909).
13. **Schauffer**, H., and **Faber**, G. B.P. 166,727 (1920).
14. **Scheibler**, H. *Ber.* **48**, 1815–26 (1915).

PETROLEUM OILS AS INSECTICIDES AND FUNGICIDES

By C. POTTER, B.Sc., D.I.C., Ph.D.

Department of Zoology and Applied Entomology, Imperial College of Science and Technology

Petroleum Oils to Control Plant Pests.

THE problem in this field is to obtain an oil and method of application which will kill the insect without damaging the plant. The oils first used were unrefined kerosines; at the present day emulsions of refined oils of relatively high boiling range have replaced them. Kerosine was first mentioned as an insecticide in 1763 [8, 1930]; it was then brushed on to the plant in an undiluted form. In 1868 [8, 1930] it was first used as an emulsion and in 1880 as a spray [12, 1933]. Kerosine emulsions were then used on dormant trees. Light to medium lubricating oils were used to some extent between 1903 and 1910 [64, 1931]. In 1905 a machine was introduced to apply oils in an atomized form [63], but it was not widely used. The lubricating oils were not commonly used until 1922. In 1926 Gray and De Ong [24] showed that the toxicity of a petroleum oil to foliage increased directly in proportion to the amount of unsaturated hydrocarbons present and that by the use of refined oils the risk of damage to plants was much lessened. Subsequent to this time the refined higher boiling-point fractions of the petroleum oils came into general use both in the winter on dormant trees and in the summer. In 1933 the use of atomized oils was revived [35], and they have since been used from aeroplanes [28, 1933] and in glasshouses [10, 1936]. The oil may be atomized undiluted or in the form of a water-in-oil emulsion. At present emulsions of oil in water sprayed on to the plant by means of a pneumatic or power sprayer is the most common method of using oils in plant protection.

Plant-feeding Insects Controlled by Petroleum Oils.

Petroleum oils belong to the class of contact insecticides, and may therefore be used against either the type of insect that feeds on the surface of the plant or the type that pierces the surface and feeds on plant juices. These oils may further be used to kill any stage of the insect from the egg to the adult. It is, however, only against certain species of insects that they have been found to be the most effective insecticides, and for some species they appear, for practical purposes, to be ineffective when used alone. In England petroleum oils are used as winter sprays against Apple Capsid *Plesiocoris rugicollis* Fall. (eggs), Common green capsid *Lygus pabulinus* Linn. (eggs), Mussel scale *Mytilaspis pomorum* Bouché (eggs), Woolly aphis *Eriosoma lanigerum* Hausm. (adults), Fruit-tree red spider *Oligonychus ulmi.* Koch (eggs), and Pear-leaf blister mite *Eryophyes pyri* Val. (adults).

In the summer in England oils may be used against Brown scale *Lecanium corni* Bouché, Mealy plum aphis *Hyalopterus arundinis* F. and the Greenhouse red spider *Tetranychus telarius* Linn.

In the United States oil sprays are used against a variety of scale insects on various plants, more particularly citrus plants. San José scale *Aspidiotis perniciosus* Coms. is one of the most important. In addition winter oils are used against the Orchard-leaf Roller *Cacoecia* (*Tortrix*) *argyrospila* Walker (eggs), Case bearers on apples, various tree hoppers, e.g. Apple-leaf hopper *Empoasca mali* le B. and Rose-leaf hopper *Empoa rosae* Linn. (eggs), European red spider *Paratetranychus pilosus* C. and F. (eggs), Clover or Brown mite *Bryobia praetiosa* Koch (eggs). In the spring oils are used against newly emerged aphides, Rosy apple aphis *Anuraphis roseus* Baker, Green apple aphis *Aphis pomi* De G., Black cherry aphis *Myzus cerasi* F., Peach aphis *Myzus persicae* Sulzer and againat onion maggot *Hylemyia antiqua* Meig. Summer oils are used against the Oriental fruit moth *Grapholita molesta* Busck, Aphids, Thrips, Leaf hoppers and red spiders, more particularly Two-spotted mite *Tetranychus bimaculatus* Harvey, and European red mite *Tetranychus telarius* Linn.

In glasshouses oils are chiefly used against Greenhouse red spider *Tetranychus telarius* Linn., but they are also used against several species of Thrips, Scale insects, and Mealy bugs.

Oils are used to kill insects present in the soil. Noble [45, 1932] recommends kerosine emulsions for sod webworms in lawns, Hammer [27, 1934] successfully applied clay emulsions of kerosine against pupae of Apple maggot *Rhagoletis pomonella*, and Wiesmann [66, 1935] completely controlled Cherry fly *Rhagoletis cerasi* L. with a mineral emulsion applied to the soil to kill the pupae. Petroleum oil is used in canker paints for Woolly aphis *Eriosoma lanigerum* Hausm. [13, 1933].

Combination of Oils with other Insecticides.

The combination of oil with another insecticide may prove more effective than either material used alone. Oil is frequently used in combination with nicotine, pyrethrum, derris, or lead arsenate. The oil-lead arsenate combination has been found to be an improvement on lead arsenate alone for the control of Codling moth *Cydia* (*Carpocapsa*) *pomonella* Linn. in America; it has the disadvantage that the oil makes the removal of the poisonous deposit of arsenate difficult. A combination of petroleum oil and tar oil has been found to be an effective winter spray in England to control the overwintering stages of the pests of fruit trees. Oil sprays are used to increase the effectiveness of hydrogen cyanide fumigation of scale insects on citrus.

Effect of Petroleum Oils on the Plant.

Where it is possible to apply oils to the plant during the winter and effectively control the insect, the risk of damage to the plant by the oil is greatly reduced, especially with deciduous plants. Oils applied in the summer are absorbed by the foliage, and damage is more likely to occur.

Oil damage can be divided into two categories: (1) acute injury (necrosis), (2) chronic injury. The first may be caused by either the light, medium, or heavy fractions of oil, and is determined more by the chemical than the physical characteristics of the oil. Gray and De Ong [24, 1926] concluded that the phytocidal properties of oils were closely correlated with their content of the more reactive constituents which are removed by sulphuric-acid treatment. No conclusive evidence is available of the exact composition of the phytocidal substances removed by refining. The symptoms of acute injury are spots on the leaves and fruit, marginal killing of the leaves, russeting of fruits, killing of lateral twigs, fruit spurs, fruit buds or branches [12, 1933].

Chronic injury is caused by the heavier refined oils and is due to metabolic disturbances caused by physical interference with the physiological process. The oil interferes with respiration and transpiration [46, 1934], the leaves may contain more chlorophyll than normal [21, 1929], and their starch content may be higher [60, 1931]. Kelly [31, 1930] found that oils decreased the transpiration rate and that the reduction was due to physical causes; he decided that the viscosity of the oil was important. Oils are absorbed principally through the under surface of the leaf [21, 1929] and may be translocated from root to leaf and vice versa [33, 1929]; these authors considered that the oils penetrated the cell, but Rohrbaugh [54, 1934] states that they were not found in cells containing protoplasm. Knight [32, 1928] found that oils of high viscosity choke the vascular system of the plant, and Young [68, 1934] states that large amounts of oils present in the parenchymatous tissues retard the diffusion of oxygen and carbon dioxide, and when present in the tracheae retard the diffusion of water. The severity of the physiological disturbances depends on (*a*) the viscosity of the oil [12, 1933; 16, 1932; 46, 1934], the more viscous oils being the most difficult to eliminate [54, 1934]; (*b*) on the amount of oil penetrating; this will be approximately the same for a given oil content since the amount evaporating before absorption is very small with insecticidal oils [33, 1929]. The resumption of normal processes is dependent on the elimination of oil from the plant tissues [7, 1929; 32, 1928; 33, 1929]. Swingle and Snapp [64, 1931] consider that the oil would be dispelled by oxidation and by means of micro-organisms; Knight, Chamberlin, and Samuels [33, 1929] state that it is deposited in the large storage cells of the pith and in the old wood fibres of the xylem.

Cumulative effects of oil sprays due to their being used too often in one season have been observed [30, 1935; 46, 1934]. The question whether oils have a cumulative effect when used over several seasons is not settled.

From these data it is evident that the least viscous oil compatible with insecticidal efficiency should be used. Symptoms of chronic injury are yellowing and fall of leaves, loss of fruit, loss of terminals. The number of fruit buds may be reduced and retarded, and the colouring of the fruits impaired [12, 1933]. After the use of summer oils the leaves may fall later than normal [21, 1929]. Oil sprays on greenhouse plants may give rise to oedema due to interference with the water metabolism of the plant. Plants vary considerably in their resistance to oil-spray damage; the nature of the resistance factors is not known. A number of external factors affect spray damage. Damage to citrus trees was greater when the trees were in need of irrigation [7, 1929]. Injury may result if rainy weather follows spraying, owing to interference with respiration at high humidities [46, 1934]. Spraying should not be done at 90° F. or higher [46, 1934] or below 40° F. [64, 1931]. Oils are liable to damage the plant when spraying is followed by severe cold [51, 1935].

Special methods have been tried to eliminate the toxic effect of the oil on the plant. Carter [9, 1934–5] used oil-charged bentonite particles. Knight and Cleveland [34, 1934] found that the glycerides of higher fatty acids or other hydroxy esters of organic acids that have a high molecular weight, and certain salts containing polyvalent cations, retard the penetration of the oil into the fruit and leaf tissue and thus increase the effectiveness of the oil film.

Effect of Petroleum Oils on Insects. Effect of Physical Properties of the Oil.

Shäfer [55, 1911] and Moore and Graham [40, 41, 1918] showed that the vapours of the more volatile petroleum oils were toxic, and Shäfer [56, 1915] and Vickering [66, 1917] considered that the vapours affected enzyme activity. Although the more volatile oils were more toxic as vapours, the high boiling-point fractions were more toxic in the form of emulsions [41, 1918]. The increasing toxicity of emulsions with increase of boiling range of the oil was also shown by Griffin, Richardson, and Burdette [26, 1927] using *Aphis rumicis*, De Ong, Knight, and Chamberlin [14, 1927], English [19, 1928], Ebeling [16, 1932] on scale insects, and Penny [49, 1932] on eggs of red spider. When using undiluted oils the most effective boiling range depends on the stage of the insect; with active adult insects (Houseflies) it was found that the more volatile fractions were the most toxic. Gibson [25, 1935] found kerosine more effective than lubricating oils to mosquito larva; using the eggs of mussel scale *Lepidosaphis ulmi* L., Pickering [15, 1906] found that the lower boiling-point fractions were ineffective owing to too rapid volatilization. The penetration of oil into the insect has been shown by Shäfer [55, 1911], adults, Nelson [44, 1927], adults, O'Kane and Baker [47, 1934; 48, 1935], eggs, and Ebeling [18, 1936], adults. These authors find that oils may sometimes be excluded by closing the spiracles and sometimes not; oils will penetrate the armour of scale insects.

Effect of Chemical Properties of the Oil.

No information is available on the toxic constituents of the vapours of petroleum oils. Using undiluted petroleum oil and its constituents on mosquito larvae Murray [42, 1936], showed that the aromatic hydrocarbons are chemically toxic; the refined oils did not show this action. When used as an emulsion on dormant stages of insects in the field, aromatic hydrocarbons in the form of tar distillates are effective in some instances, and only petroleum oils with a high percentage of unsulphonatable residue in others. Against the eggs of *Cheimatobia brumata* [66, 1927], *Plesiocoris rugicollis* [61, 1930], and *Lygus pabulinus* [2, 1934; 3, 1935] it was shown that a certain percentage of saturated hydrocarbons was essential, and the relative ineffectiveness of the tar distillate sprays on scale insects compared with saturated petroleum oils is shown by Hough [29, 1932]. On the other hand, tar distillates are effective against the eggs of Aphididae and Psyllidae which are not affected by the saturated petroleum oils, and Sleesman [57, 1935] found that dipping the eggs of *Hylemyia antiqua* in undiluted oil for 60 minutes did not reduce the rate of hatching. Austin, Jary, and Martin [2, 1934] showed that the action of petroleum oils on the eggs of *Lygus pabulinus* was independent of the base of the oil.

Mode of Action of Petroleum Oils.

The available evidence indicates that the paraffinic and naphthenic constituents of petroleum oils have little or no chemical toxic action; the aromatic and olefinic constituents are actively toxic but may not be used in foliage sprays owing to their phytocidal properties.

Staniland, Tutin, and Walton [61, 1930] postulate a stifling action for the saturated hydrocarbons and a chemical action for the aromatic compounds, but there is still very little detailed evidence on this subject, most of the data available being obtained from observations of the action of oil emulsions in the field.

Specification of Oil to use on Plants.

The type of oil to use depends first on whether the tree is dormant or active, and it is possible to spray dormant deciduous trees more drastically than dormant evergreens. A summary of the factors involved in drawing up a specification of an insecticidal oil is given by Martin [37, 1935]: the characteristics to be stated are (*a*) distillation range, (*b*) viscosity for physical characteristics, (*c*) unsulphonated residue or iodine value as a chemical criterion. From a consideration of the available data Martin tentatively specifies a winter oil satisfying the following criteria: *Sp. gr.* (60° F.) 0·86–0·92; *Boiling range* at least 90% by vol. to distil above 315° C.; at least 50% by vol. to distil above 350° C., at least 20% by vol. to distil above 380°C.; *Viscosity* Redwood no. 1 at 70° F. ≮ 125 sec. and ≯ 500 sec.; *Unsulphonated residue* ≮ 60% by vol. The oil should yield 100% neutral oils and be free from alkali. Not enough evidence is available on the other physical and chemical properties of the oil to make a useful statement.

For a summer oil for use on deciduous trees and herbaceous plants Martin suggests the following specification: *Sp. gr.* (60° F.) 0·86–0·92; *Boiling range* ≮ 90% of the oil distil above 300° C., ≮ 10% below 330° C., ≮ 50% of the oil should distil above 340° C. and below 365° C.; *Viscosity* Redwood no. 1 at 70° F. approx. 75 sec. minimum (equiv. approx. to 60 sec. Say. at 100° F.) and 150 sec. maximum (approximates to 110–120 sec. Say. at 100° F. indicated by Americans); *Unsulphonated residue* ≮ 90% (Americans indicate ≮ 85%).

Further characteristics have been suggested as being significant from time to time: (*a*) volatility, (*b*) pour and cold tests, (*c*) base of oil, (*d*) colour, (*e*) solubility in dimethyl sulphate, (*f*) sludge test, (*g*) sulphur content. Martin considers that on the available evidence those that are not covered by the specifications given are not proved important. The iodine value (Hüble or Wijs) or the heat of bromination may be used instead of the unsulphonatable residue in the specification.

The evidence on which these tentative specifications are drawn up is set out by Martin [37, 1935] and is derived from laboratory and field-spraying trials on insects and plants using oil emulsions. They are based on the fact that these trials have shown that for insecticidal efficiency the oil must be above a certain minimum viscosity and unsulphonatable residue; any oil conforming to these criteria can be used as a dormant spray on deciduous trees. For use on foliage the oil must have a much higher minimum unsulphonatable residue to prevent chemical damage to the plant and as low a viscosity as possible to prevent physical damage.

Emulsions.

Emulsions of oils for use as insecticides are prepared in four ways [38, 1936]:

(*a*) Tank mixture methods where the oil is vigorously agitated in the spray tank with water and an emulsifier unaffected by hard water, e.g. blood albumen, triethanolamine.

(*b*) Two solution methods where a suitable liquid fatty acid, e.g. oleic acid, is dissolved in the oil and this solution is added to a dilute solution of alkali, thus producing an emulsion.

(*c*) Stock emulsions: these are made by processing the oil-water-emulsifier mixture in an emulsifying mill. The emulsifiers used may be soaps or non-soaps, or finely divided materials.

(*d*) Miscible oils are solutions of the emulsifier in the oil, complete solubility usually being obtained by the use of a mutual solvent such as cresylic acid or amyl alcohol.

Stock emulsions may cream or break on exposure to frost; miscible oils are unsuitable for use with abnormally hard or saline water. Miscible oils have the advantages of stability during storage and on exposure to frost, ease of handling, and high oil content. Swingle and Snapp [64, 1931] found the particle size of an emulsion from a miscible oil to be 1–2 μ, from boiled soap stock = 3–5 μ, from cold soap stock 4–6 μ, and from non-soap 9–15 μ.

Griffin, Richardson, and Burdette [26, 1927], using aphids, found that the toxicity of lubricating oil and kerosine emulsions varied with droplet size, droplets of 8–12 μ being more effective than 2–3 μ and less, and this low toxicity persists regardless of oil base, viscosity, or other physical characteristics of the oil. With larger droplet size more oil is retained on the plant. English [19, 1928] confirmed Griffin, Richardson, and Burdette's results on droplet size. The rate of breaking summer oil emulsions is important [35, 1933]. De Ong and colleagues showed that with a given oil content the toxicity of an emulsion increased as the emulsifier content was decreased. This relationship between concentrations of emulsifier and insecticidal efficiency was confirmed by Smith [58, 1932] Ebeling [16, 1932], and Cressman and Dawsey [11, 1934].

When using winter washes against eggs the stability of the emulsion does not appear to affect markedly the ovicidal efficiency [1, 1933; 59, 1934; 62, 1932].

Use of Oils in Household Sprays.

This is an important use of oils as insecticides; they are not, however, the main toxic agent but are partly carriers and partly accessory toxic agents. Primary toxic agents used are pyrethrum, derris, and the thiocyanates. A complete account of household sprays containing pyrethrum is given by Gnädinger [23, 1936]. Atomized oil sprays are used in houses against adult flies and mosquitoes and against clothes moths; they may be used against bed bug. No generally accepted data is available as to the most toxic oil to flies. Richardson [53, 1932] found that within a boiling range of 150–270° maximum toxicity occurred in fractions 207–260°. Murphy and Peet [43, 1934], using the oils as carriers, found light volatile carriers the best. The type of oil has been largely regulated by the necessity in houses of having a volatile carrier which will evaporate completely, leaving no stain. The standard oil used in America as a carrier when testing fly sprays has the following specification [4, 1935]: A.P.I. gravity 49–50; Flash-point, open cup, 120° F.; Initial boiling-point 350° F.; End-point 510° F.; Saybolt colour = 30+, odour slight; Iodine number Hanus < 1.

The oil base for sprays against clothes moths are similar but somewhat more volatile; flash-point 115–125° F. open cup and distillation range over 325° F. initial to 450° F. end. These sprays may have up to 60% carbon tetrachloride to prevent fire risk [5, 1936].

Use of Oils in Medical Entomology.

Oils are used to destroy the larvae and pupae of mosquitoes of various species, chiefly in the prevention of disease transmission. Mosquito larvae and pupae are aquatic, and the oils are applied by distributing the oil on the surface of the water. Murray [42, 1936] has summarized the position and has thrown light on a number of problems. Oils penetrate the air tubes of the insects when they rise to the surface to breathe. Oils of boiling range 200–300° C. are the most effective; above this range the oils are too viscous to penetrate, below this range they are too volatile and the insect reacts to prevent penetration.

According to Murray [42, 1936] the aromatic hydrocarbons and phenols when added are the actively toxic constituents of the petroleum oils, the paraffinic hydrocarbons having a physical action only; however, once penetration is effected the insect invariably dies, so that mode of toxic action is not an important factor. Old films of oil were found not to penetrate as well as fresh films. Gibson [25, 1935], under field conditions, found that the addition of derris powder to an emulsion of oil with soap increased its effectiveness against the larvae of *Aëdes*.

Use of Oils in Warehouses.

Oils are used against insects attacking stored foodstuffs. Flint and Mohr [20, 1930] prevented injury to stored maize by dipping in lubricating oil emulsions. Mackie [36, 1932] used dormant spray oils with success to destroy grain weevils, *Calandra granaria*, in empty warehouses. Potter [50, 1935], using a solution of pyrethrum in a highly refined white oil, obtained complete protection of stored goods from the Indian meal moth *Plodia interpunctella* Hb. and the cacao moth *Ephestia elutella* Hb. With Potter's method the object of the process is to form a film over all exposed surfaces; this can be done by spraying the surfaces directly with the oil atomized by compressed air, or by putting up a mist in the warehouse by special atomizing apparatus; the settling of the mist forms a film. The film of pyrethrum in oil is lethal to the adults and larvae of the pests and prevents their reaching the stored food. This process has been used to a considerable extent in Britain. An oil for this purpose must be non-volatile so that there is no fire risk and it will form a permanent film, and it must be odourless and tasteless so that it does not taint. The following are tests of an oil fulfilling these criteria: *Sp. gr.* 0·862; *Flash-point closed* 320° F.; *Flash-point open* 335° F.; *Viscosity* Redwood no. 1 at 70° F. 118 sec.; *Pour test* 30° F., and sufficiently refined to be odourless and tasteless.

Use of Oils as Stock Sprays.

Oils are used to prevent flies attacking dairy cattle. Attacks of stable fly *Stomoxys calcitrans* result in reduced milk production. Regan and Freeborn [52, 1936] summarize the effect of oils on the cow. Oil may result in reduction of yield of milk, the body temperature and respiration may be raised, and skin-burning results with oils of < 40 sec. viscosity irrespective of sulphonatable residues. Unsulphonatable residues below 90% are dangerous in oils of viscosity > 65 sec. Oil impairs the ability of the skin to maintain the body temperature, affects water loss and lowers the pyrexial point. These authors consider that a water emulsion of pine oils, pyrethrum, and small amounts of petroleum oils is better than an undiluted oil spray. A spray for use on cattle should have no detrimental physiological effect; it should also have repellent as well as toxic properties to the flies. The following is a specification for an oil recommended for use in stock sprays [6, 1936]: *Viscosity* Saybolt no. 1 at 100° F. 45–50 sec.; flat distillation curve, most of the oil distilling between 550° and 650° F. and with an end-point $\ngtr$ 700° F.; *Sulphur content* $\ngtr$ 0·4%; *Unsulphonatable residue* $\nless$ 70%. If the oil is too light it burns the cattle, due to solvent and penetrating properties; if it is too heavy it interferes with the physiological processes.

Use of Oils as Fungicides.

Kerosine emulsions and the highly refined lubricating oils have been used as fungicides [38, 1936]. However, Martin and Salmon [39, 1931] showed that the vegetable oils were more fungicidal and less phytocidal than the petroleum oils. Petroleum oils are frequently used in combined washes of insecticide and fungicide, or are used in fungicidal sprays to increase penetration and retention of the spray materials.

REFERENCES

1. Austin, M. D., Jary, S. G., and Martin, H. *J.S.E. Agric. Coll. Wye*, **32**, 63 (1933).
2. —— —— —— *J. South East Agric. Coll. Wye*, **34**, 114–35 (1934).
3. —— —— —— *J. South East Agric. Coll. Wye*, **36**, 86–94 (1935), 5 refs.
4. Anon. *Soap Blue Book* (1935).
5. —— *Soap* (March 1936).
6. —— *Soap* (1936).
7. Brock, A. A. *Mon. Bull. Dept. Agric. Calif.* **18**, 572–3 (1929).
8. Browne, A. C. *Mon. Bull. Dept. Agric. Calif.* **19**, no. 6 (1930).
9. Carter, W. *Science*, **80**, 315 (1934).
10. Craig, J. W. *The Fruit Grower* (March 1936).
11. Cressman, A. W., and Dawsey, L. H. *J. agric. Res.* **49**, 1–19 (1934).
12. Cunningham, G. H., and Muggeridge, J. *N.Z. J. Agric.* **47**, 8–18, 89–96 (1933), 35 refs.
13. Denny, A. A. *Proc. Ent. Soc. Brit. Columbia*, no. **30**, 8–10 (1933).
14. De Ong, E. R., Knight, H., and Chamberlin, J. C. *Hilgardia*, **2**, no. 9 (1927).
15. Bedford, Duke of, and Pickering, S. U. *6th Rep. Woburn Exp. Fruit Farm*, 75 (1906).
16. Ebeling, W. *J. econ. Ent.* **25**, 1007–12 (1932).
17. —— *J. econ. Ent.* **28**, 728–9 (1935).
18. —— *Hilgardia*, **10**, 95–125 (1936).
19. English, L. L. *Ill. Nat. Hist. Survey*, **17**, 235–59 (1928).
20. Flint, W. P., and Mohr, C. O. *Ill. Agric. Exp. Sta. Bull.* no. **359**, 376–88 (1930).
21. Ginsburg, J. M. *J. econ. Ent.* **22**, 360–6 (1929), 11 refs.
22. —— *J. agric. Res.* **43**, 469–74 (1931).
23. Gnadinger, C. B. *Pyrethrum Flowers*, Minneapolis (2nd ed. 1936).
24. Gray, G. P., and De Ong, E. R. *Ind. Eng. Chem.* **18**, 175–80 (1926).
25. Gibson, A. New Jersey Mosquito Extermination Assoc. *Proc. 22nd Ann. Meeting*, 77–91 (1935).
26. Griffin, E. L., Richardson, C. H., and Burdette, R. C. *J. agric. Res.* **34**, 727 (1927).
27. Hammer, O. H. *J. econ. Ent.* **27**, 291–2, 367–9 (1934).
28. Herbert, F. B. *J. econ. Ent.* **26**, 1052–6 (1933).
29. Hough, W. S. *J. econ. Ent.* **25**, 613–17 (1932).
30. —— *J. econ. Ent.* **28**, 1075 (1935).
31. Kelley, V. W. *Ill. Agric. Sta. Bull.* **348** (1930).
32. Knight, H. *Science*, **68**, 572 (N.Y., 1928).
33. Knight, H., Chamberlin, J. C., and Samuels, C. D. *Plant Physiology*, **4**, 299–321 (1929).
34. Knight, H., and Cleveland, C. R. *J. econ. Ent.* **27**, 269–89 (1934).
35. Le Pelley, R. H. *Bull. Ent. Res.* **24**, 2–32 (1933).
36. Mackie, D. B. *Mon. Bull. Dept. Agric. Calif.* **21**, 474–88 (1932).
37. Martin, H. *Ann. appl. Biol.* **22**, 334–414 (1935). 74 refs.
38. —— *Scientific Principles of Plant Protection* (2nd ed. 1936).
39. Martin, H., and Salmon, E. S. *J. agric. Sci.* **21**, 638 (1931).
40. Moore, W. S., and Graham, S. A. *J. econ. Ent.* **11**, 70–5 (1918).
41. —— —— *J. Agric. Res.* **13**, 523–38 (1918).

42. Murray, D. R. P. *Bull. ent. Res.* **27**, 289–305 (1936).
43. Murphy, D. F., and Peet, C. H. *Soap*, **10**, 95, 97, 99, 101, 103 (1934).
44. Nelson, F. C. *J. econ. Ent.* **20**, 632–5 (1927).
45. Noble, W. B. *U.S. Dept. Agric. Circ.* no. **248**, 4 pp. (1932).
46. Newcomer, E. J. *Proc. 5th Pacific Sci. Congr.* **4**, 3419–22 (1934).
47. O'Kane, W. C., and Baker, W. C. *N.H. Agric. Exp. Sta. Tech. Bull.* **60**, 1–12 (Durham, N.H., 1934).
48. —— —— *N.H. Agric. Exp. Sta. Tech. Bull.* **62**, 8 pp. (1935), 16 refs.
49. Penny, D. D. *J. econ. Ent.* **25**, 1002–7 (1932).
50. Potter, C. *Ann. appl. Biol.* **22**, 769–805 (1935).
51. Reed, L. W. *J. econ. Ent.* **28**, 379–85 (1935).
52. Regan, W. M., and Freeborn, S. B. *J. Dairy Sci.* **19**, 11–28 (1936).
53. Richardson, H. H. *Ind. Eng. Chem.* **24**, 1394–7 (1932).
54. Rohrbaugh, P. W. *Plant Physiol.* **9**, 699–730 (1934).
55. Shäfer, G. D. *Mich. Agric. Coll. Expt. Sta. Tech. Bull.* **11** (1911).
56. Shäfer, G. D. *Mich. Agric. Coll. Expt. Sta. Tech. Bull.* **21** (1915).
57. Sleesman, J. P. *J. econ. Ent.* **28**, 453–7 (1935).
58. Smith, R. H. *Bull. Calif. Agric. Exp. Sta.* **527** (1932).
59. Speyer, W. *Z. angew. Ent.* **20**, 565 (1934).
60. Spuler, A., Overley, F. L., and Green, E. L. *Washington Agric. Exp. Sta. Bull.* no. **247**, 27 pp. (1931).
61. Staniland, L. N., Tutin, F., and Walton, C. L. *J. Pomology*, **8**, 129–52 (1930).
62. Steer, W. *Ann. Rep. East Malling Res. Sta.* 132 (1932).
63. Strawsón, G. F. *Insects and Fungi Injurious to Plants*, Part 2 (Spottiswoode & Co., 1905).
64. Swingle, H. S., and Snapp, O. I. *U.S. Dept. Agric. Tech. Bull.* no. **253**, 48 pp. (1931), 126 refs.
65. Tutin, F. *Ann. Rep. Agric. and Horti. Res. Sta., Long Ashton, Bristol* (1927).
66. Vickering, R. K. *Calif. Comm. Hort. Mo. Bull.* **6**, 384–7 (1917).
67. Weismann, R. *Anz. Schädlingskunde*, **11**, 97–103, 110–15 (1935).
68. Young, P. A. *J. agric. Res.* **49**, 559–71 (1934).

SYNTHETIC RESINS FROM PETROLEUM HYDROCARBONS

By CHAS. ALLEN THOMAS, A.B., D.Sc., A.I.C.E.

Director of Research, Thomas and Hochwalt Laboratories, Research Division, Monsanto Chemical Company

With the advent of high-octane gasolines, produced by cracking operations under conditions more severe than had theretofore been used, it was observed that the resulting distillates deposited a greater amount of so-called gum than had former motor fuels. Apparently this gum started to form in storage and its formation was accelerated by the heat of the motor. In one method of largely overcoming this difficulty the gasoline is subjected to a mild acid treatment to remove the most drastic of the gum-forming constituents without removing excessive amounts of unsaturated compounds to which the fuel owes some of its high anti-knock character. In another method, anti-oxidants and antipolymerizing catalysts are added to retard the formation of this gum.

Exactly contrary to this modern development, a study was undertaken shortly thereafter to produce a distillate with the maximum amount of gum-forming constituents and to determine the cracking conditions most favourable for their production. The goal of this research was to produce plastic products of commercial value. The result has been the development of a new type of resin, quite different from the tacky gums of foul odour at that time known to the petroleum industry. This resin, known to the plastic industry as Santoresin is a hard, brittle, light-coloured, oil-soluble, odourless, fusible substance.

Prior to the inception of this research, gummy masses had been produced by the action of oxidizing agents or adsorbent earths. The products varied from tacky oils to black asphaltic pitches and were used in road-binders and for other similar purposes in which a low-grade tar or binder could be utilized.

It has been generally accepted that gums are largely a function of the diolefine content of the distillate. On the other hand, a highly cracked distillate contains gum-forming hydrocarbons other than diolefines. Examination of many types of distillates produced under various cracking conditions in this work revealed that high temperatures and low pressures were, in general, the best conditions for producing a resin-forming distillate. Such distillates contained straight-chain and cyclic olefines, straight-chain and cyclic diolefines, aromatic and substituted aromatic hydrocarbons with both saturated and unsaturated side chains, and some unchanged paraffin hydrocarbons.

Many types of catalysts were investigated to learn their function in polymerization of the resin-forming hydrocarbons contained in such highly cracked mixtures. It was concluded that a metallic halide was the most advantageous since it promotes both condensation and polymerization reactions [6, 1932].

In the manufacture of resins from cracked petroleum distillates, rigid specifications are maintained upon the cracking operation and its products. Boiling ranges, specific gravities, refractive indices, and average molecular weights are some of the determinations that are made on each sample of distillate obtained. The composition, that is, the content of aromatic, monolefine, and diolefine hydrocarbons, is determined by the usual methods. If a particular distillate fails to meet the required specifications it can be blended with another distillate or its deficiencies can be corrected by the addition of various substances; for example, if the content of monolefines is low, a definite amount of amylene or other monolefine can be added [9, 1934]. After meeting the specifications the distillate is immediately converted into resin, for it has been observed that there is a tendency for oxidation and polymerization to proceed if left in storage.

In reacting such a distillate with aluminium chloride the following four main reactions are believed to take place:

(1) Polymerization of olefines to form high-boiling oils.
(2) Combination of olefines with aromatics to form substituted aromatics.
(3) Polymerization and condensation of diolefines and olefines to resins.
(4) Combination of diolefines with substituted aromatics and subsequent polymerization of these products to resins.

In the following discussion of these reactions it should be pointed out that the rates of these reactions are at present unknown, but through a study of each individual reaction the course of the reactions that occur in a highly cracked distillate can be deduced.

Reaction (1). The polymerization of olefines by a metallic halide has been well reviewed by Sullivan and his co-workers [1, 1931]. Lubricating oils are prepared by this method which are claimed to have superior qualities. This reaction alone is detrimental in the formation of resins, as high-boiling oils reduce the melting-point of the resins and cause them to be tacky. It also retards the drying and adhesiveness of a varnish made from such a resin. However, olefines must be present in the distillate to take part in reactions (2) and (3).

Reaction (2). Olefines in the presence of aromatics when treated with aluminium chloride form substituted aromatics. For example, *p*-amyl toluene is formed from amylene and toluene. A part of the olefines present in the distillate described react to form branched-chain aromatics [4, 1934]. The reaction does not stop with the monosubstituted compound, but, if there is an excess of olefines present, di- and tri- substitutions may take place. Also, the amount of aluminium chloride is a factor in this reaction.

Reaction (3). When a very pure diolefine, such as isoprene, is treated with aluminium chloride, no violent reaction takes place, as was commonly supposed. However, if a small amount of olefine is present with the diolefine, reaction starts immediately and continues violently. If a pure diolefine, such as isoprene, is in contact with aluminium chloride, no temperature-rise or other obvious chemical reaction is observed, even when a considerable portion of the anhydrous aluminium chloride has been added [8, 1933]. After leaving pure isoprene in contact with anhydrous aluminium chloride for several hours, small bubbles appear around the aluminium chloride particles. These bubbles are followed later by a spongy polymeric growth. In a few days masses of this light-yellow polymer, which is apparently insoluble in the remaining water-white isoprene, form. After weeks the greater proportion of the isoprene is slowly converted into this gelatinous polymer, which, when washed and purified, is found to have the formula $(C_5H_8)_x$. This polymer is insoluble in practically all organic solvents. For this reason its molecular weight has not been determined. The polymer is slightly soluble in nitrobenzene and some of the higher amines. Strong acetates decompose the product and phenols react with it, giving a reddish coloration accompanied by some decomposition. By slowly heating the polymer it starts to depolymerize around 116° C., undergoing some peculiar physical changes. First it contracts and becomes more spongy and rubbery, then upon continued heating to 300° C. its colour changes to brown and the particles slowly fuse, with some foaming, to a transparent darker resin. This resin is soluble in most hydrocarbon and chlorinated hydrocarbon solvents. However, when an equimolecular mixture of isoprene and an olefine such as pentene-2 or trimethyl ethylene is polymerized with aluminium chloride, a violent reaction takes place. This reaction can be controlled by adding the aluminium chloride in small portions with agitation and drastic cooling [6, 1932]. A point is soon reached after which further additions of aluminium chloride cause no additional evolution of heat. When the aluminium chloride complex is decomposed, for example, by the addition of ammonia, it is found that two polymers result, one soluble and the other insoluble in organic solvents. The insoluble polymer is precisely that previously described, whereas the soluble polymer may vary from a viscous oil to a hard resin, depending upon the proportion of olefines and diolefines employed and the subsequent treatment to which the product is subjected. If the oil is removed, there results a hard resin which ranges in colour from a light straw to a dark brown. This resin is soluble in most hydrocarbon solvents and drying oils such as linseed and china wood oil. It is virtually insoluble in methyl and ethyl alcohol, which precipitate it from solutions in hydrocarbons, but it is somewhat soluble in the higher alcohols and acetates. This soluble polymer behaves somewhat like a drying oil when spread over a surface in a thin film. On standing in the air its iodine value gradually decreases and its acid value, which was formerly approximately 0, slowly rises with the decrease in iodine number.

By varying the proportion of olefine polymerized with the diolefine, various amounts of the two polymers can be obtained. This is shown in Fig. 1, in which pure pentene-2 was polymerized with varying molecular proportions of isoprene, the hardness of the soluble polymer also being shown. The ordinates of this curve are reciprocals of the penetration value as measured by the A.S.T.M. penetration apparatus. It can be seen that the hardness of the polymer rapidly decreases with the amount of pentene-2 in the mixture. In a cracked distillate containing diolefines and olefines, this general type of reaction takes place. When an excess of olefines is present, the resulting resin is very soft, being sometimes only a semi-viscous oil. In this case practically no insoluble polymer is formed. The hardness of the resin, therefore, can be controlled by adding diolefines to such a mixture. If it is observed that a large amount of insoluble polymer is formed with a particular mixture, the yield of soluble polymers can be increased by the addition of olefines.

Reaction (4). It has been found that diolefines react with substituted aromatic hydrocarbons, a reaction which is probably similar to that of the combination of olefines with aromatics. However, the intermediate products from the diolefines polymerize to resins in the presence of the aluminium chloride complex. Here again two polymers are formed—a soluble and an insoluble. When studying pure compounds in this type of reaction, it has been found that the more substituted the aromatic nucleus, the greater is the tendency for reaction to take place. In fact, no appreciable amount of resin is formed from a diolefine and pure benzene. Some general observations are of interest in the case of isoprene with various substituted aromatics. Xylene is the simplest di- substituted benzene containing two methyl groups, and it has three isomers. When the three xylenes are respectively polymerized with a diolefine such as isoprene, the para-xylene yields the smallest proportion of resin. However, this resin has the highest melting-point and is lighter in colour than that obtained from either ortho- or meta-xylene, which produce higher yields of resin, but the resin has a slightly darker colour. When benzene is substituted with higher molecular weight alkyl groups, the yield of resin is greater and the colour is lighter. The more branched the chain in the alkyl substituent, the more noticeable is the above effect.

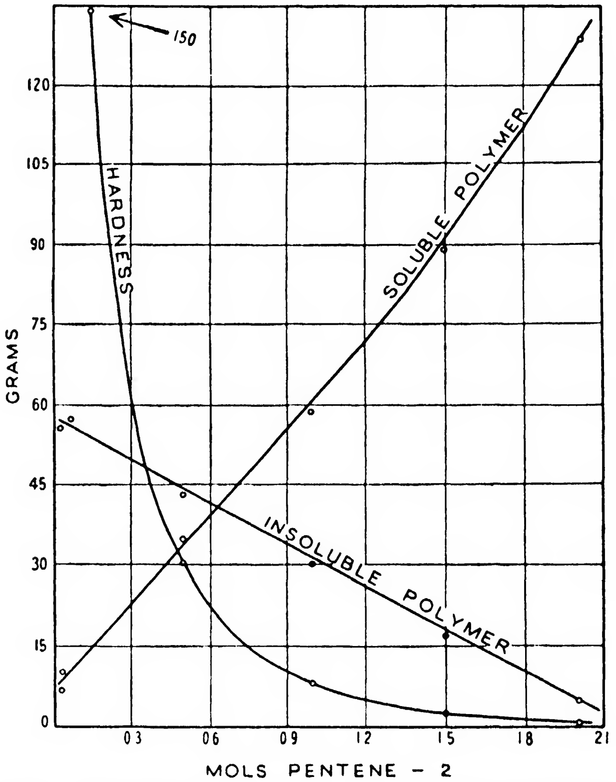


FIG. 1. Relationship of two polymers when pentene-2 is added to isoprene.

It should also be pointed out in the discussion of the four general reactions that although straight-chain olefines and diolefines were taken as examples, it has been found that cyclic olefines and cyclic diolefines follow the same general reactions. However, with cyclic compounds the reaction is much more vigorous and the resulting resin is harder and of a better character [5, 1934].

Manufacture of Santoresin

Fig. 2 is a flow sheet of the resin manufacturing process. A photograph of the apparatus in which these operations are conducted is shown in Fig. 3. Polymerization is carried out in vessels equipped with adequate cooling means [10, 1931]. Since the reaction is highly exothermic, the anhydrous aluminium chloride is added in a finely divided state in a small continuous controlled stream. The distillate darkens as polymerization continues and has a dark reddish-brown colour at the end of the reaction. The specific gravity of the distillate increases as polymerization continues. Thus, by determining the specific gravity as reaction progresses the degree of polymerization can be ascertained. When the reaction is completed no further rise in specific gravity occurs even upon further addition of catalyst. The reaction mixture is then treated with a suitable alkali to break down the aluminium chloride complex, while the hydrocarbon resin remains in solution. On the addition of alkali, aluminium hydroxide and alkali chloride are precipitated, together with a small amount of insoluble polymer. In the manufacture of soluble resin, however, the proportion of this polymer is reduced to a minimum by control of raw materials, according to the principles described before [9, 1934]. On the other hand, in the manufacture of insoluble polymer, the raw material is adjusted to the production of a large yield of insoluble and a small yield of soluble polymer. The inorganic material is separated from the resin in solution by filtration. By repeatedly treating the solid residue with dilute acid and subsequent washing, the inorganic salts are washed out, leaving the white granular insoluble polymer [9, 1934].

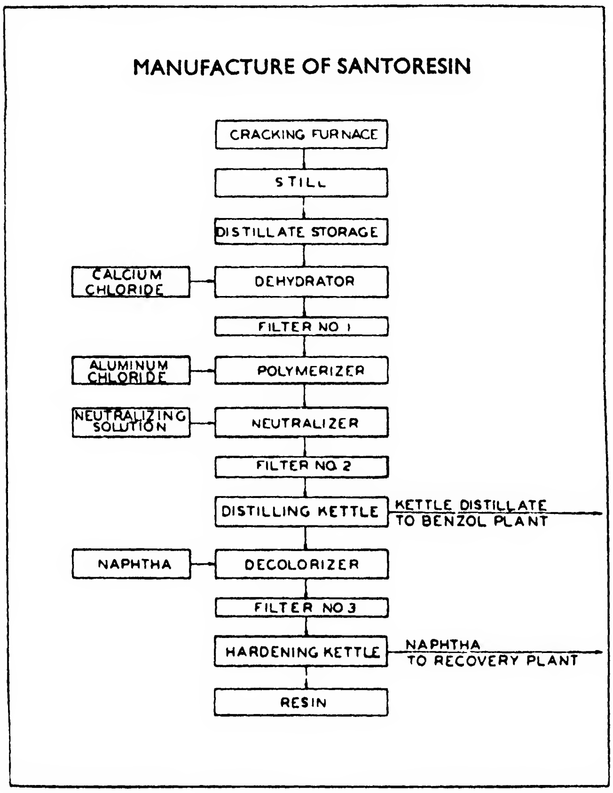


Fig. 2.

The soluble polymer left in the filtrate is recovered by removing the solvents by distillation at as low a temperature as possible. Vacuum distillation is usually employed. The last traces of high-boiling oils are removed by passing superheated steam directly into the hot molten resin. Up to certain limits the hardness of the resin is controlled by means of this addition of superheated steam. The melting-points of varnish resins produced by this process can be varied, according to the use to which the product is to be subjected, from about 110 to 150° C.

The characteristics of the hydrocarbon resins in varnishes are worthy of note. It has been found that the drying-rate of china wood oil varnishes is largely dependent upon the type of resin used in their preparation [11, 1932]. Oil varnishes made with neutral resins dry faster than those made from acid resins. Hydrocarbon resins in general are neutral and therefore give very fast-drying varnishes. Because of their hydrocarbon nature, these resins are highly resistant to alkali, water, and acid. Most resin varnishes on exposure darken by actinic rays. However, varnishes made with Santoresin exhibit a tendency to bleach on exposure to light.

These resins also find application in moulded products. For this purpose they are milled with an inert filler such as wood flour, cotton linters, or the like. The moulding mixture thus prepared is then moulded under heat and pressure. Articles moulded from these resins are thermoplastic, that is, they can be reshaped by reheating and pressing. However, when sulphur is added to the moulding mixture a true thermo-setting compound results, which is completely hardened by moulding under heat and pressure.

In this brief account the possibilities of petroleum as a starting-point for organic syntheses has been indicated. Rapid advances are being made in this new industry created by the discovery of these methods of preparing resins from a raw material as abundant as petroleum.

REFERENCES

1. Sullivan, F. W., Jr., Voorhees, V., Neeley, A. W., and Shankland, R. V. *Ind. Eng. Chem.* **23**, 604–11 (1931).
2. Thomas, C. A. U.S.P. 1,939,932 (1933).
3. —— U.S.P. 1,940,613 (1933).
4. —— U.S.P. 1,947,626 (1934).
5. —— U.S.P. 1,982,707 (1934).
6. Thomas, C. A., and Carmody, W. H. *J.A.C.S.* **54**, 2480–4 (1932).
7. Thomas, C. A., and Carmody, W. H. *Ind. Eng. Chem.* **24**, 1125–8 (1932).
8. —— —— *J.A.C.S.* **55**, 3854–6 (1933).
9. —— —— U.S.P. 1,982,708 (1934).
10. Thomas, C. A., and Hochwalt, C. A. U.S.P. 1,836,629 (1931).
11. Thomas, C. A., and Marling, P. E. *Ind. Eng. Chem.* **24**, 871–3 (1932).

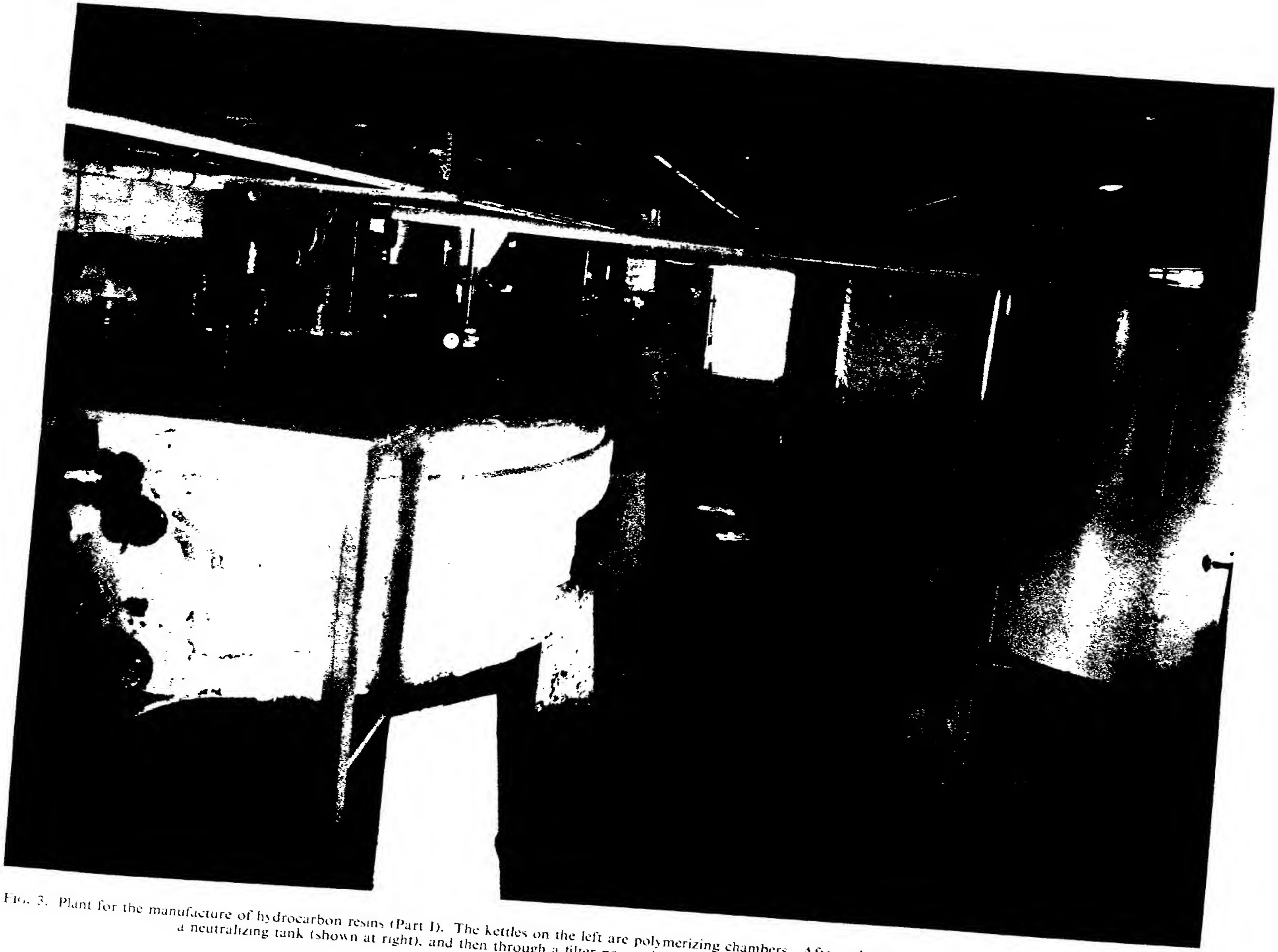


Fig. 3. Plant for the manufacture of hydrocarbon resins (Part I). The kettles on the left are polymerizing chambers. After polymerization in these kettles the batch is passed to a neutralizing tank (shown at right), and then through a filter press (shown at rear), from where it is passed to a storage tank

CARBON-BLACK MANUFACTURE

By CARLETON ELLIS

Industrial Research Chemist

Classification

THE classification of blacks, which consist of substantially pure carbon, into two main divisions, carbon black and lampblack, is dependent upon the method of deposition. Carbon black (also called natural-gas black, gas black, hydrocarbon black, ebony black, Paris black, and channel black) is thus regarded as the product resulting from the impingement of a flame of natural or other hydrocarbon gas on a surface (generally metallic) and lampblack, that deposited as a soot in the incomplete combustion of a solid or liquid organic substance in free space (i.e. without impingement). Such a classification is neither complete nor satisfactory [8, 1912; 29, 1922; 37, 1931].

The division of blacks on the basis of their method of manufacture, as proposed by D. S. Chamberlin and A. Rose [10, 1929], is somewhat more explicit. These methods are as follows:

1. **Incomplete Combustion with Impingement.** A hydrocarbon gas, burning in a limited supply of air, is allowed to impinge on a hot depositing surface which is at a temperature much lower than that of the impinging flame and which may be termed 'cool'. The earliest methods for the manufacture of carbon black from natural gas, such as the channel and roller processes, which are described later, were of this type. In point of production these are still the most important.
2. **Thermal Decomposition.** A hydrocarbon gas or atomized oil is subjected to thermal decomposition in the absence of air. This class is at present the second largest source of carbon black, and the 'Thermatomic' process, which is subsequently described, is typical. In this process, however, only hydrocarbon gases are employed.
3. **Explosion.** A hydrocarbon gas, such as acetylene, is exploded in a limited supply of air. Acetylene black is made by this method. This type of operation has not attained any great importance in the United States, although in Europe some acetylene black is manufactured from the carbide scrap.
4. **Incomplete Combustion without Impingement.** A liquid or solid hydrocarbon is burned in a limited supply of air to produce soot, which is collected. Lampblack is manufactured in this way. Under this heading is also included the Lewis process, described later, in which the fumes resulting from incomplete combustion of natural gas are sprayed with water and, from the slurry thus formed, the carbon is separated.
5. **Destructive Distillation.** Organic materials are distilled, leaving residues of charcoals or cokes which are subsequently pulverized for use. Petroleum coke, which is discussed in another section of this book, results from such treatment. These substances, however, should not be confused with carbon blacks.

Mechanism of Carbon-black Formation

The production of carbon black by incomplete combustion of gases containing hydrocarbons is not the result of preferential oxidation of the hydrogen of the hydrocarbon, but is a direct thermal decomposition [29, 1922]. Part of the gas burns, producing oxides of carbon, and the heat liberated is sufficient to cause the decomposition of another part of the hydrocarbon gas into carbon and hydrogen. Essentially, therefore, the method is similar to that of thermal decomposition (method 2), except that in the latter the heat is furnished by an external source.

W. A. Bone and his collaborators [3, 1915; 4, 1927] pointed out that the thermal decomposition of methane is a purely surface effect, giving rise to a hard graphitic carbon, but the decomposition of ethane, ethylene, and higher hydrocarbons takes place throughout the entire mass of the gas, leading to a soft form of carbon. It is well known that unsaturated hydrocarbons, such as ethylene and acetylene, can be formed by incomplete combustion of methane or its homologues, and consequently there is a possibility that these unsaturated hydrocarbons, and not methane itself, are the generators of the finely divided carbon black.

The thermal decomposition of methane furnishes carbon and hydrogen, according to the reaction:

$$CH_4 \rightarrow C+2H_2.$$

The carbon produced in this way, however, was heretofore of a low grade [29, 1922], hence such reactions were principally used as sources of hydrogen. But, for hydrogen production, they are inferior to decomposition with steam [11, 1934], which reactions may be represented with methane as follows:

$$CH_4+H_2O \rightarrow CO+3H_2$$
$$CH_4+2H_2O \rightarrow CO_2+4H_2.$$

From 1 volume of methane, therefore, only 2 volumes of hydrogen can result by simple thermal decomposition, whereas 3 or 4 are possible by reaction with steam.

Most hydrocarbons require a high temperature for decomposition into carbon and hydrogen. Acetylene, however, is an exception, its dissociation being exothermic and explosive. Explosion processes (method 3 above), therefore, appear to be simple thermal decompositions, a small quantity of energy initiating the decomposition, which subsequently proceeds under its own evolution of heat. Obviously, explosion methods can only be used with acetylene or gases of a similar exceptional exothermic nature.

Incomplete Combustion with Impingement

The processes for the manufacture of carbon black by incomplete combustion with impingement, or, as it can also be considered, deposition from flames, differ principally in the shape of depositing surface. Natural gas is the hydrocarbon mixture generally used, and flat flames are best. The relative proportions of gaseous paraffin hydrocarbons present in natural gases are of special importance in black manufacture. In general, a gas containing a moderate proportion of ethane is better than one which is entirely methane [29, 1922].

The yield depends upon the process used and the type of product desired, and is only slightly affected by the composition of the gas. It generally varies from ½ to about 2 lb. of black per 1,000 cu. ft. of natural gas, although 31·82 lb. of carbon are theoretically obtainable from 1,000 cu. ft. of methane [28, 1932].

G. C. Lewis [27, 1928] has shown from pyrometric measurements that the natural gas flame temperature varies from 1,000 to 1,200° C. Temperatures of hydrocarbon gas flames have also been determined by a number of other workers [19, 1931; 20, 1931; 24, 1928]. W. B. Wiegand [37, 1931] studied the characteristics of a round and a flat or 'bat-wing' type of flame and the factors which influence quality and yields. The carbon black obtained from round flames was characterized by a greyer colour, lower oil absorption, increased flow characteristics, greater miscibility in rubber, but diminished reinforcing effects (tensile strength and elongation) in rubber compositions. A flat flame is essential, and for that purpose bat-wing burners, which are slotted, or fish-tail burners, with two opposing jets, are used.

The depositing surface serves two purposes [29, 1922]. In the first place, the liberated carbon is cooled somewhat so that no oxidation changes, or agglomeration of particles, from prolonged heating can take place. Secondly, the carbon is maintained at high enough temperature for sufficient time to calcine it or free it from occluded matter. Thus, deposited carbon can also be regarded as being baked, and impingement processes, therefore, as baking processes. The temperature of the depositing surface should normally not exceed 500° C. (W. B. Plummer and T. P. Keller [31, 1930] give 516° C. as the optimum temperature for the production of black from propane.) Too cool a surface prevents the maximum separation of carbon.

In the so-called *channel process*, first used by L. J. McNutt [26] in 1892, a system of iron channel beams is used as the depositing surface. These channel beams are turned with the flat side downwards over a horizontal row of stationary burners and are given a slow reciprocating motion. From these beams the black is scraped off and removed by spiral conveyers.

In the *roller process*, which is still used to make small quantities of blacks for lithographic and embossing inks, printing inks for half-tone engravings, and other special purposes, a burner giving a rounded flame is so placed that its flame impinges on a cast-iron cylindrical roller rotating at a slow speed. This is known also as the 'Peerless' process.

The *rotating-disk process*, in which the depositing surface is a cast-iron disk of about 3 ft. diameter supported on a central mast rotating with it, has been superseded to a great extent by the channel process.

A report of yields, compiled in 1922 by R. O. Neal [29, 1922], though these have been increased in most plants since that time and vary with the field, may serve as a basis of comparison of these impingement processes (Table I).

TABLE I

Yields of Carbon Black by Various Processes

Process	*Carbon blacks lb. per 1,000 cu. ft. of gas*
Channel	0·78 to 1·40
Roller	0·80
Rotating disk	0·95 to 1·40

The average yield by the channel process since 1922 in the United States has been increasing steadily, from 1·40 lb. per 1,000 cu. ft. in 1929 to 1·44 in 1931 [15]. In comparison it is to be noted that the Thermatomic process, which is described next, is capable of giving consistent yields of 9 lb. of a form of soft carbon by the thermal decomposition of 1,000 ft. of natural gas [2]. This material differs in physical properties from channel black and should not be substituted for it.

According to D. S. Chamberlin and A. Rose [10, 1929], the principal factors affecting the yield and quantity of the carbon black produced by incomplete combustion of natural gas are (1) composition of gas, (2) rate of burning, (3) nature of burner tips, (4) pressure of gas, (5) position of plate in flame, (6) draught conditions, (7) material of plate, (8) motion of plate, (9) shape of plate, (10) humidity of atmosphere, (11) barometric pressure, (12) temperature of gas, (13) temperature of plate, and (14) uniformity of operating conditions. Dependent upon some or all of these factors are (*a*) the height of the flame, and (*b*) the composition and (*c*) temperature of the atmosphere in which the flame burns. Burner tips made of lava, a selected steatite, are generally favoured [29, 1922].

Regulation of the air supply is controlled empirically by the 'smoke blanket', the blackish haze that should appear approximately on the level of the channel irons, and by the colour of the smoke issuing from the buildings. If the smoke blanket rises or falls, draughts are adjusted to bring it back to its normal position. Admission of too much air will result in too hot a flame, which, as has been mentioned previously, will cause a larger proportion of the carbon to be burned, whereas too cool a flame will not give sufficient decomposition and deposition. With too cool a flame, moreover, the deposited carbon is likely to be contaminated with intermediate combustion products.

Although the industry is almost entirely confined to burning of natural gas, because of the cheapness of this gas, consideration has been given to other materials as well. For example, studies have been made on the products resulting from the burning of acetylene [1, 1897], propane [31, 1930], diacetylene [16, 1930], and other hydrocarbon mixtures [11, 1934].

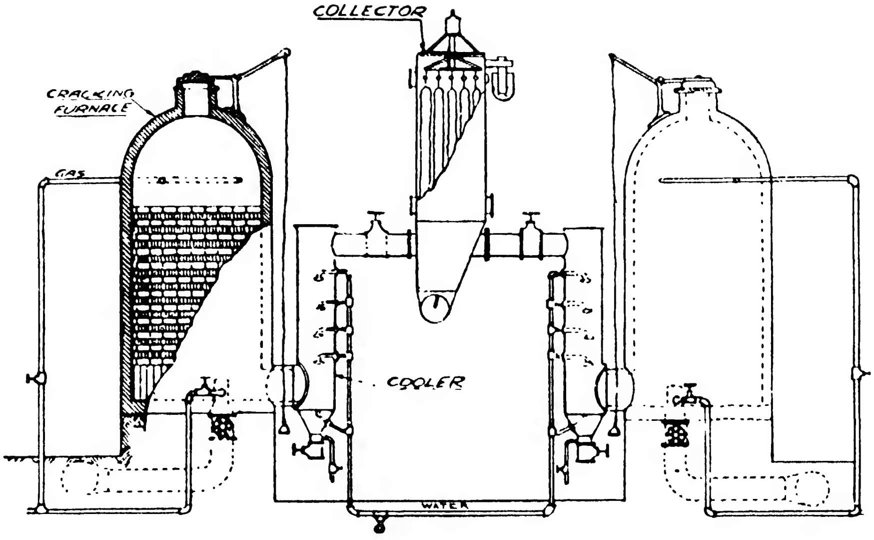
Thermal Decomposition

From about 1912 attempts have been made to produce carbon black by the thermal decomposition of hydrocarbons. These numerous proposals have been described elsewhere [11, 1934]. As mentioned previously, the carbon black resulting from such processes has been of an inferior quality, but with the development of the processes of R. H. Brownlee and R. H. Uhlinger [5, 1916], which are the basis of the Thermatomic process, carbon blacks made by this method have won a position of increasing importance in the market.

The *Thermatomic process* consists in heating to incandescence a furnace (lined with refractory brick and filled with checkerbrick) by an upward blast of natural gas and air, shutting off the air, and allowing the natural gas (admitted from the top at this stage) to decompose. The intermittent heating and cracking operations (the latter being endothermic) are carried out alternately, each charge lasting about 5 minutes [28, 1932]. Fig. 1 is a diagram of the plant which has been developed, consisting essentially of two cracking furnaces, two coolers, and one collector.

Approximately two-thirds of the total carbon black produced is deposited on the refractory material. Such carbon is valueless and is left in the furnace to be consumed in the next air blow. It is stated [6, 1923] that the best operating temperature for the cracking process is 1,200 to 1,400° C., and the gas mixture is subjected to these temperatures for a period of 3 to 4 seconds only.

On issuing rapidly from the furnace, the mixture of gases and carbon is passed through a cooling chamber where just



Courtesy Industrial and Engineering Chemistry

FIG. 1. General arrangement of plant for thermal decomposition of hydrocarbons (Thermatomic process)

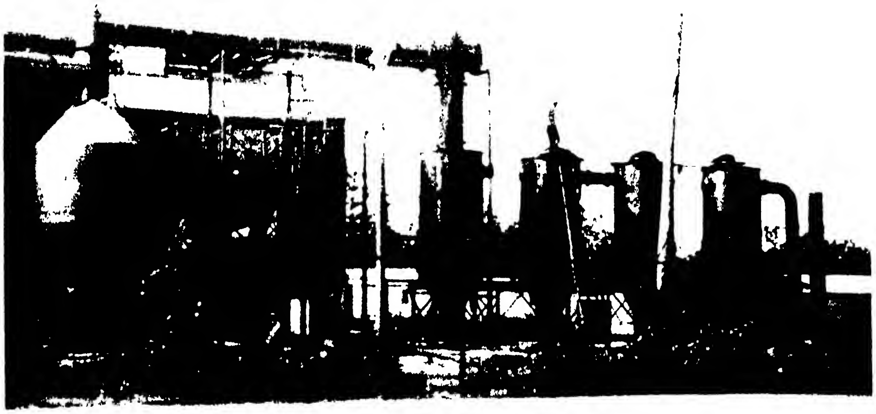
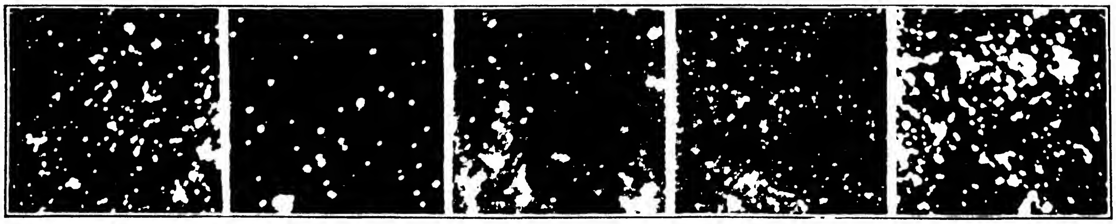


FIG. 2. Lewis Wet Process Black Plant, Hancock, Louisiana



Courtesy Industrial and Engineering Chemistry

Charlton Micronex Super Spectra Thermatomic Goodwin

FIG. 3. Photographs of Blacks at × 860

enough water is sprayed countercurrent to the gas stream [7, 1924] to cool the smoke to a safe temperature for filtering through cloth bags without leaving an excess to wet either the bags or the carbon.

This process has been producing the carbon called Thermatomic or Thermax since 1922. Later, another type, 'P-33', which is blacker and finer, was put on the market. P-33 is made in the same way as Thermatomic or Thermax, except that a portion of the resulting gas containing 80% hydrogen is recirculated and acts as a diluent for the decomposing natural gas. This dilution is so effective, according to R. E. Moore, that it reduces the average particle size to about one-fifth that of Thermax [28, 1932; 34, 1931].

Explosion

Although carbon blacks can be made from acetylene by the same methods that are used for their manufacture from natural gas, acetylene is exceptional, as heretofore mentioned, in that it decomposes explosively into carbon and hydrogen. This explosion can be brought about by heating with or without air, usually under pressure, or by an electric spark. Acetylene black, as the carbon made from acetylene is designated, is produced in Germany, France, and Canada [21, 1933], the source of the acetylene being refuse calcium carbide. Like carbon blacks made from natural gas, the properties vary, depending upon the method of manufacture, i.e. whether the acetylene is burned as in the channel process (disintegrated by heat) or decomposed by explosion.

Incomplete Combustion without Impingement

Lampblacks continue on the market, but such products are generally made from coal-tar oils, such as creosote dead oil, and hence are not of concern to the petroleum chemist. One plant, however, in which natural gas is burned and the black is not deposited by impingement is in operation. This plant uses the *G. C. Lewis* [22; 23, 1931] *process*, in which the gas, under regulated conditions, is led into a number of burners in a furnace lined with fire-brick. The height of flame is adjusted to the grade of black required. The fumes, which consist of carbon, complex hydrocarbons, and an appreciable percentage of steam, leave the top of the furnace and pass to collectors, where they are sprayed with water. The slurry resulting from the washing is pumped to large settling tanks with conical bottoms in which the carbon settles and is drawn off and separated in filter-presses. The filter-cake is then dried and pulverized. The combustion chamber and spray tanks used in this process are shown in Fig. 2.

This wet method is said to remove occluded matter from the black and reduce its bulk to a minimum. Furthermore, as the tanks accumulate the products of several days' operation, the black is extremely uniform. The oil which floats on the surface of the water in the settling tanks contains varying amounts of naphthenes, nitrobenzene, and cyanogen compounds.

Properties of Carbon Black

Carbon black is a black velvety powder with an extremely low apparent specific gravity. The particles of which this powder is composed are below the resolving power of the microscope in size, the indications being that they do not exceed 0·1 to 0·2 micron (0·0001 to 0·0002 mm.) on the average [12*a*, 1932], but because of their tendency to agglomerate this figure may be low [13, 1928]. In Fig. 3 are reproduced photomicrographs of several carbon blacks. To this extremely fine state of subdivision are to be attributed its remarkable properties.

Because of their fineness, carbon blacks always occlude gases, particularly oxygen, nitrogen, and oxides of carbon. This occlusion has been studied by G. A. Hulett and H. E. Cude [29, 1922] and by C. R. Johnson [17, 1928].

The crystalline structure has been examined by a number of investigators [11, 1934]. Although the consensus of opinion is that both carbon black and charcoal are essentially graphitic in nature, the evidence is not altogether convincing and authorities are not in complete agreement. However, W. B. Plummer [30, 1930] and H. H. Lowry [25, 1924] support the view that the so-called amorphous carbons consist of unsaturated hydrocarbons of very high molecular weight and highly deficient in hydrogen, i.e. carbon complexes in which the fields of force between the carbon atoms are unbalanced by an occasional stray hydrogen atom, thus preventing crystallization (graphitization) and producing a general state of unsaturation and, hence, high surface activity.

The heats of combustion of carbon blacks and various other forms of elemental carbon have been determined by W. A. Roth and O. Doepke [32, 1927] and W. B. Plummer [30, 1930]. The latter investigator observed that the heat of combustion of carbon black (8,272 cal. per g.) which has been degassed at 1,000° C. is higher than that of graphite (7,932 cal. per g.) or any other form of elemental carbon. Prolonged heating at 1,000° C. or higher results in a gradual lowering of the heat of combustion, which is ascribed to slow crystallization (graphitization).

Ultimate analyses show that carbon blacks contain substances other than carbon. Appreciable proportions of volatile and small proportions of mineral matter are usually present. In good-grade blacks, however, the mineral (ash) content is extremely low. In Tables II and III are given the compositions of various carbon blacks, lampblacks, and other carbons. Although there is a possibility that the values given in Table III are not entirely representative, they indicate the general trend of the differences between the compositions of carbon blacks made by various processes.

Uses of Carbon Black

For centuries lampblack has been produced in China, Egypt, and elsewhere [27, 1928; 35, 1926]. Since 1864, when carbon black made its appearance, lampblack has been replaced to a very great extent by carbon black. The latter is now indispensable in the manufacture of inks. Certain blacks produce the so-called short inks (i.e. inks of buttery consistency which do not flow rapidly) used in lithographic and offset work, in slow-speed presses, and for most half-tones. Other blacks can be used in so-called long inks (i.e. inks which do not string when drawn between the fingers), which, because of their more rapid flow and opacity, are employed in fast-running presses. However, it should be noted that in the largest application of carbon blacks in ink, i.e. in news ink for high-speed presses, short channel blacks are used, since news inks are not made with a varnish base as are book inks, but with rapid-drying, free-flowing petroleum oils.

The next great application of carbon black began about 1915 when it was first added to rubber. Because of its unique reinforcing properties in rubber compositions, it has almost completely displaced zinc oxide as a filler in the rubber industry. In tire treads, proportions up to 45% of the rubber or 27 to 28% of the final composition are added.

TABLE II

Analyses of Various Carbon Blacks, Lampblack, and other Blacks [29, 1922]

Carbon	Method of manufacture	Proximate analysis				Ultimate analysis					Real specific gravity (dry basis)
		Water %	Volatile matter %	Ash %	Fixed carbon %	H %	C %	N %	O %	S %	
Auk carbon black	Channel	2·64	7·06	0·00	90·30	0·59	95·04	0·06	4·31	0·00	1·85
Kalista carbon black (long black)	Roller	5·30	10·40	0·14	84·16	0·55	92·91	0·08	6·30	0·01	1·88
New Vulcan carbon black (short black)	Rotating disk	3·12	5·58	0·08	91·22	0·72	96·64	0·05	2·51	0·00	1·78
Carbon from thermal decomposition of methane	High temperature decomposition	0·02	0·78	0·84	98·36	0·45	98·72	0·01	..	0·05	..
	Lower temperature decomposition	1·25	6·40	0·24	92·11	1·13	97·99	0·01	0·51	0·12	..
American lampblack	Incomplete combustion of oil	3·12	17·38	0·06	79·44	1·20	90·67	0·00	7·41	0·66	..
Cracked natural gas black	Heated retort	0·02	0·78	0·84	98·36	0·45	98·72	0·01	..	0·05	1·72
Willow charcoal		3·24	14·66	1·87	80·23	2·46	87·89	0·17	7·47	0·08	..
Bone black		3·88	10·92	82·52	2·68	0·47	8·99	1·10	3·53	0·06	..

TABLE III

Proximate Analyses of Carbon Blacks

Carbon black	Method of manufacture	Specific gravity	Moisture %	Volatile matter %	Ash %	Ref. No.
Auk	Channel	1·85	2·64	7·06	0·00	[29]
Micronex	Channel (for rubber)	1·79	2·80	..	0·01	[13]
Super Spectra	Channel (for varnishes)	1·89	5·70	..	0·08	[13]
Kalista (long black)	Roller	1·88	5·30	10·40	0·14	[29]
New Vulcan (short black)	Rotating disk	1·78	3·12	5·58	0·08	[29]
Thermax	Thermatomic	1·80	0·25	..	0·05	[28]
P-33	Thermatomic (gas recycle)	1·80	0·25	..	0·15	[28]
Acetylene black	Explosion	1·89	0·06	1·0	0·03	[21]
Fumarex	Lewis process	1·8+	<1·0	1·0	<0·1	[22]
Charlton	Oil black	1·66	2·90	..	0·08	[13]
Goodwin	Incomplete combustion at high temperature	1·82	0·08	..	0·04	[13]

Some realization of its importance in such uses may be gained from the statement that the incorporation of black increased the life of a tire from 5,000 miles to about 20,000 miles. Besides its toughening characteristics, it appears to protect the rubber substance from the effects of light and may retard oxidation [29, 1922].

Carbon black is finding increasing application as a pigment in various paints and enamels. It has a higher tinting strength than any other black, but lacks the clear bluish tone of lampblack, and is generally acknowledged to be superior for varnishes and enamels. Both long and short carbon blacks ordinarily possess a reddish-brown undertone which can be partially corrected by the use of blue dyes ('toners'), but which renders these blacks unsatisfactory for certain inks. Acetylene black and lampblacks, on the other hand, have a blue undertone [20, 1931].

Carbon black also is employed because of its intense blackness and high colouring power, fine state of division, and low cost, for example, in stove and shoe polishes, carbon paper, phonograph records, and medical hard rubber. However, the question of economics plays some part in deciding between the use of lampblack and carbon black. The relative development of the natural-gas industry in the United States and of the coal-tar industry in Europe creates an economic urge towards the use of carbon black in the United States and lampblack in Europe, whenever possible.

The production and utilization of carbon black in the United States is best summarized in the Government statistics [15] given in Table IV.

TABLE IV

Production of Carbon Black in the United States

Year	1930	1931	1932	1933	1934	1935
Number of producers reported .	33	26	24	25	25	21
Number of plants	69	58	50	51	50	54
Production (thousands of pounds):						
By channel process . .	350,254	255,322	224,536	238,026	293,546	316,284
By other processes . .	29,688	25,585	18,164	35,099	35,282	36,465
Total . .	379,942	280,907	242,700	273,125	328,828	352,749
Quantity sold (thousands of pounds):						
Domestic						
To rubber companies . .	128,572	134,315	130,380	191,358	165,446	213,708
To ink companies	19,220	15,184	18,341	18,539	16,146	15,177
To paint companies . .	11,922	6,760	7,636	6,260	5,365	6,550
For miscellaneous purposes .	7,565	5,453	5,126	6,025	5,035	9,916
Exported . .	84,260	96,714	100,072	152,286	120,620	142,185
Total . .	251,539	258,426	261,555	374,468	312,612	387,536

It was mentioned that the first great application of carbon black, in printing ink, was a result of its pigmenting characteristics. Its second application, in rubber, which accounted for 80% of the American sales in 1932, was attributed to its reinforcing properties. Though this second outlet occurred literally in spite of its colour, W. B. Wiegand and J. W. Snyder [38, 1934] believe that its third great utilization will be in the newer black lacquers, again dependent upon its pigmenting characteristics.

Testing of Carbon Black

G. St. J. Perrott [29, 1922] described a number of physical and chemical tests which may be used for determining the characteristics of a sample of carbon black and its probable value for various purposes. Other methods have been outlined by N. Goodwin and C. R. Park [13, 1928]. Some of these tests are briefly outlined below.

Moisture. The moisture content is determined by heating a sample of the black for 1 hour at 105° C. in a constant-temperature oven in circulating dry air. It should not exceed 4 or 5%.

Ash. The ash content is determined by ignition of a sample to cherry-red heat (about 750° C.). The maximum for most purposes should be about 0·2%.

Solvent Extract. Extraction can be made with acetone [13, 1928] or, as preferred by some, with benzene [2]. N. Goodwin and C. R. Park [13, 1928] attach little importance to this test, since the extractable matter appears to bear no direct relation to the quality and because of the impossibility of accurately determining the total extractable matter.

Results of some of these tests on various carbon blacks have already been given in Table III.

The adsorptive capacity of carbon blacks can be measured by using solutions of benzoic acid [9, 1929], iodine [13, 1928], dyes [33, 1926] (e.g. methylene blue), oils [13, 1928], hexamethylenetetramine [33, 1926], alkalis [36, 1929], diphenylguanidine [36, 1929], and acetic acid [12, 1930]. The correlation of such data with the action of carbon blacks in rubber mixes, for example, has led to some confusion, many workers maintaining that no general relationships exist.

Other tests, such as the estimation of tinting power, colour, grit, and hiding power or spreading rate, are empirical, but are valuable in deciding the possible application of the black. The colour and tinting power of carbon blacks have been correlated with other physical properties by G. St. J. Perrott [29, 1922], C. R. Johnson [18, 1927], L. Hock [14, 1928], N. Goodwin and C. R. Park [13, 1928], and W. B. Wiegand and J. W. Snyder [38, 1934].

Extent of the Industry

The extent of the carbon-black industry can be judged both from the production figures given in Table IV and from the fact that it consumed 14% of the total natural gas used in 1929. About 87% of the gas which was burned for carbon black that year was stripped for gasoline. The natural-gas gasoline and carbon-black industries are complementary. The carbon-black industry is dependent upon the availability of large supplies of cheap natural gas. Where higher-priced uses are found for the gas, the industry has had to move. Thus, about 1920, it migrated from West Virginia into Louisiana and, about 1928, into its present location in the Panhandle (Texas) district. In 1929 the industry was located largely in Texas and Louisiana, less than 3% of the total output representing the combined production of West Virginia, Wyoming, Oklahoma, Montana, and Kentucky [15].

REFERENCES

1. Berger and Wirth. G.P. 92,801 (1896); *Chem. Zentr.* 1897 (2), 688.
2. Boardman, C. C. Private communication.
3. Bone, W. A., Davies, H., Gray, H. H., Henstock, H. H., and Dawson, J. B. *Phil. Trans. Roy., A*, **215,** 275–318 (1915).
4. Bone, W. A., and Townend, D. T. A. *Flame and Combustion in Gases* (Longmans, Green & Co., New York, 1927).
5. Brownlee, R. H., and Uhlinger, R. H. U.S.P. 1,168,931 (1916). See Ellis for further bibliography.
6. —— —— U.S.P. 1,478,730 (1923).
7. —— —— U.S.P. 1,520,115 (1924).
8. Cabot, G. L. *Reports Eighth Internat. Congress Applied Chem.* **12,** 13–31 (1912).
9. Carson, C. M., and Sebrell, L. B. *Ind. Eng. Chem.* **21,** 911–14 (1929).
10. Chamberlin, D. S., and Rose, A. *Trans. Amer. Inst. Chem. Eng.* **22,** 155–64 (1929).
11. Ellis, C. *The Chemistry of Petroleum Derivatives* (Chemical Catalog Co., Inc., New York, 1934), 1285 pp.
12. Fromandi, G. *Kautschuk*, **6,** 27–30 (1930).

12*a*. Gehman, S. D., and Morris, T. C. *Ind. Eng. Chem.*, Anal. Ed., **4,** 157–62 (1932).

13. Goodwin, N., and Park, C. R. *Ind. Eng. Chem.* **20,** 621–7 (1928).
14. Hock, L. *Kautschuk*, **4,** 266–8 (1928).
15. Hopkins, G. R., and Backus, H. *Minerals Yearbook* (various years), U.S. Government Printing Office.
16. I. G. Farbenindustrie A.-G. B.P. 357,749 (1930).
17. Johnson, C. R. *Ind. Eng. Chem.* **20,** 904–8 (1928).
18. Johnson, C. R. *India Rubber World*, **77** (5), 65–6 (1927).
19. Jones, G. W., Lewis, B., Friauf, J. B., and Perrott, G. St. J. *J.A.C.S.* **53,** 869–83 (1931).
20. Jones, G. W., Lewis, B., and Seaman, H. *J.A.C.S.* **53,** 3992–4001 (1931).
21. Kaufmann, C. *Chem. Markets*, **33** (3), 217–20 (1933).
22. Lewis, G. C. Private communication.
23. —— U.S.P. 1,801,436 (1931).
24. Loomis, A. G., and Perrott, G. St. J. *Ind. Eng. Chem.* **20,** 1004–8 (1928).
25. Lowry, H. H. *J.A.C.S.* **46,** 824–46 (1924).
26. McNutt, L. J. U.S.P. 481,240 (1892).
27. Mantell, C. E. *Industrial Carbon* (D. Van Nostrand Co., Inc., New York, 1928), 410 pp.
28. Moore, R. L. *Ind. Eng. Chem.* **24,** 21–3 (1932).
29. Neal, R. O., and Perrott, G. St. J. *U.S. Bureau Mines Bulletin*, **192,** 1–95 (1922).
30. Plummer, W. B. *Ind. Eng. Chem.* **22,** 630–2 (1930).
31. Plummer, W. B., and Keller, T. P. *Ind. Eng. Chem.* **22,** 1209–11 (1930).
32. Roth, W. A., and Doepke, O. *Ber.* **60,** 530–6 (1927).
33. Spear, E. B., and Moore, R. L. *Ind. Eng. Chem.* **18,** 418–20 (1926).
34. —— —— U.S.P. 1,794,558 (1931).
35. Wiborg, F. B. *Printing Ink* (Harper, New York, 1926), 299 pp.
36. Wiegand, W. B. *Canad. Chem. Met.* **13,** 269–70 (1929).
37. —— *Ind. Eng. Chem.* **23,** 178–81 (1931).
38. Wiegand, W. B., and Snyder, J. W. *Ind. Eng. Chem.* **26,** 413–19 (1934).

PART IV

DETONATION AND COMBUSTION

SECTIONS 41 and 42

SECTION 41

COMBUSTION

COMBUSTION PHENOMENA OF HYDROCARBONS

By D. M. NEWITT, D.Sc., and D. T. A. TOWNEND, D.Sc.
Imperial College of Science and Technology

A. SLOW COMBUSTION

Introduction.

DURING the greater part of last century the study of hydrocarbon combustion was concerned principally with efforts to ascertain whether one or other of the elements constituting the hydrocarbon molecule burned preferentially; and it was not until W. A. Bone and his collaborators (1898–1905) had shown that a whole series of intermediate compounds were formed which subsequently gave rise to the end products—oxides of carbon and steam—that the complexity of the oxidation was recognized and the first comprehensive theory of hydrocarbon combustion was formulated [11, 1927]. The contemporaneous development of the internal-combustion engine and the subsequent growth of the oil industry have stimulated interest in the subject and have led during the past 30 years to numerous investigations covering nearly every phase of hydrocarbon chemistry.

In spite of the mass of experimental data that has accumulated, however, there is still some difference of opinion as to its interpretation, and there remain gaps in our knowledge which make it difficult to write a connected story embodying all the known facts. In reviewing the evidence as a whole, data have to be co-ordinated relating to substances belonging in some cases to the same homologous chemical series but differing widely in physical properties, thermal stability, and resistance to oxidation; and it has to be borne in mind that certain phenomena which are pronounced features of the combustion of members in one part of a series may be imperceptible or indeed absent in another part of the same series. Moreover, it is now known that comparatively small variations in reaction temperature and/or pressure may influence profoundly the course of combustion. Failure to give due weight to these considerations is responsible for many of the apparently contradictory statements found in the literature.

All hydrocarbons will, under suitable conditions of temperature and pressure, unite slowly with oxygen without formation of flame and with no appreciable rise of temperature. The products consist mainly of the two oxides of carbon, steam, aldehydes, and acids, but no free carbon or hydrogen; in addition alcohols and substances of peroxydic character are found together with a variety of other products due to secondary reactions.

The rate of such slow reactions conforms to no simple 'order' of reaction but increases very rapidly with increasing hydrocarbon concentration and is relatively little influenced by changes in the oxygen concentration; the most reactive mixture is usually that containing hydrocarbon and oxygen in the ratio 2 : 1. It is also found that the temperature of initial combustion in air (i.e. the lowest temperature at which steam, carbon dioxide, and aldehydes can first be detected in the products) varies with mixture strength and has a minimum value for mixtures containing an excess of hydrocarbon over the theoretical amount for complete combustion.

Thus Callendar and Mardles found the following values for ethylene-air mixtures, the period of heating being about 20 sec. [14, 1927].

The Temperature of Initial Combustion of Ethylene-Air Mixtures

Mixture strength % by volume of combustible:	1·9	3·0	5·4	7·5	18	24	31	37	43	56	64	78
Temp. of initial combustion ° C.:	540°	535°	530°	515°	505°	490°	480°	464°	459°	453°	465°	468°

With increasing molecular weight the lowest temperature of initial combustion of the paraffin decreases at first but tends to a constant value. In the following table are given data relating to (*a*) the paraffins, (*b*) aromatic hydrocarbons, (*c*) various aldehydes and alcohols, (*d*) fatty acids.

TABLE I

Lowest Temperature of Initial Combustion in Air of Certain Organic Substances (Callendar and Mardles)

Substance	*Mixture strength g. of combustible per 100 g. of mixture*	*Temp. initial combustion ° C.*
(*a*) Methane	..	615
Ethane	..	542
n-Pentane	21	295
iso-Pentane	26	303
n-Hexane	23	265
Octane	..	215
Nonane	..	210
Decane	..	210
(*b*) Benzene	18·5	670
Toluene	9·5	550
Xylene	5·2	540
Naphthalene	..	580
(*c*) Methyl alcohol	15	440
Ethyl alcohol	8	445
Amyl (*iso*) alcohol	7	450
Butyl alcohol	42	570
Benzyl alcohol	5	390
Paraldehyde	8	220
Formaldehyde	4	300
Acetaldehyde	38	185
Propyl aldehyde	19	135
Valeraldehyde	6·5	230
(*d*) Acetic acid	12	450
Formic acid	1·5	200

Another characteristic of the reactions is that when any hydrocarbon-oxygen medium is introduced into an enclosure maintained at such a temperature that oxidation will eventually take place, there is a delay or 'induction' period during which there is no measurable pressure-change in the system and little or no combination takes place; this is succeeded by a period of relatively rapid reaction during which the greater part of the hydrocarbon or oxygen, whichever is in defect, is consumed.

The durations of the 'induction' and 'reaction' periods are found to depend upon such factors as the temperature and pressure of the system, the relative proportions of hydrocarbon and oxygen, the dimensions and nature of the surface of the enclosure, and to be influenced by the presence of traces of certain substances such as nitrogen peroxide, aldehydes, and alcohols (Bone [6, 1932]).

The extent to which the relative proportions of hydrocarbons and oxygen influence the induction and reaction periods may be seen from the data given in Table II. These facts and many others lead to the view that the hydrocarbon molecule is oxidized in definite stages, each one being marked by the formation and subsequent oxidation or thermal decomposition of an intermediate oxygenated derivative, the final products being the oxides of carbon and steam; the number of stages will increase with the complexity of the molecules, and it is only in the case of the simpler members of the paraffin, olefine, and acetylene series that some of the principal intermediate compounds have been identified and information obtained as to the order of their appearance.

TABLE II

Durations of Induction and Reaction Periods in the Slow Combustion of Hydrocarbon-Oxygen Mixtures (Bone [6])

Hydrocarbon Temperature ° C.	*Methane* 447°			*Ethane* 316°			*Propane* 267°			*Ethylene* 300°	
Hydrocarbon-oxygen ratio	2 : 1	1 : 1	1 : 2	2 : 1	1 : 1	1 : 2	2 : 1	1 : 1	1 : 2	2 : 1	1 : 1
Duration of											
(1) 'Induction' (min.)	3·5	10	18	3	30	60	110	170	700	16	47
(2) 'Reaction' (min.)	35	400	*	13	35	225	14	21	32	11	33

* Too long to be measurable.

The Mechanism of Exothermic Reactions.

Before attempting to survey the experimental evidence upon which the foregoing résumé is based, some account must be given of the mechanism of exothermic reactions. It will be recalled that according to the view first put forward by Arrhenius collision between molecules leads to reaction only when their combined energies exceed a certain value (E) called the 'activation energy'. At any temperature (T) the fraction of molecules with energy exceeding E is $e^{-E/RT}$. The velocity constant k of the reaction will therefore be given by $k = Ce^{-E/RT}$, and the temperature coefficient of reaction rate by

$$\frac{d\log k}{dT} = \frac{E}{RT^2}.$$

When the reaction is slow, the heat liberated is largely dispersed by conduction and convection; but as the velocity increases a point is reached at which the rate of heat liberation exceeds that of its removal, the temperature of the system will then rise rapidly and the reaction may become explosive. Such in its simplest form is the thermal view of the genesis of an explosion.

There are a number of phenomena of slow and explosive combustion, however, which are not adequately explained on the above hypothesis. Thus, for example, the well-defined 'induction' period, the effect of pressure upon the limits of inflammation, and the action of certain classes of substances in inhibiting combustion all point to the existence of specific conditions of energy transfer more or less independent of temperature. Such considerations have led to the suggestion that combustion in general proceeds by a 'chain' mechanism [20, 1928, 1932; 52, 1935]. It is postulated that when reaction occurs between suitably energized molecules the heats of 'activation' and 'reaction' are not transferred by molecular collisions to the system as a whole, thereby causing a general temperature rise, but by specific encounters with suitable reactant molecules which hand on the energy quantum wise. In this way the rate of reaction is related to the number and length of the so-called chains. In the case of the hydrocarbons the sequence of reactions which occur during oxidation require a modification of this mechanism. We may suppose that during the oxidation of the original molecule R, which is relatively resistant to oxidation, a less stable intermediate oxygenated compound Y is formed. The further oxidation of Y may then, by furnishing a supply of oxygen atoms, accelerate the first stage, thus setting up a chain of reactions somewhat as follows:

$$\begin{aligned} &Y+O_2 \rightarrow YO+O \\ &O+R \rightarrow Y \\ &Y+O_2 \rightarrow YO+O, \text{ \&c.} \end{aligned}$$

In certain circumstances chains may divide or branch, thus setting up fresh centres of activity; for example, the further oxidation of the product YO may create a new source of oxygen atoms, thus:

$$YO+O_2 \rightarrow YO{:}O+O.$$

The number of active centres will tend to increase except in so far as deactivating processes such as molecular collisions may preserve a balance; and since the rate of production of active centres and the rate of deactivation depend, *inter alia*, upon concentration, there will be a pressure limit at which the former exceeds the latter, and the reaction rate will undergo a sudden acceleration resulting, in suitable circumstances, in inflammation of the medium.

Reaction chains may both originate and terminate on the walls of the containing vessel; in the latter event the reaction rate will be found to be influenced by the dimensions of the vessel and will be retarded by increasing the surface; also, the introduction of an inert gas may, by hindering the chains reaching the walls, accelerate the reaction. We may therefore accept as criteria of chain reactions one or more of the following: (1) the occurrence of an induction period during which reaction is very slow, followed by (2) an abrupt change to rapid and maybe explosive combustion, (3) acceleration of the reaction by addition of an inert gas, and (4) dependence of rate of reaction on the dimensions of the vessel and its surface-volume ratio.

The Combustion Characteristics of some Typical Hydrocarbons.

We may now proceed to consider in more detail the behaviour of some typical gaseous and liquid hydrocarbons. There are two methods in general use for studying their slow combustion, namely, a 'static' method in which the reacting medium is introduced into a closed vessel, maintained at some suitable temperature, and connected with a manometer, and the progress of oxidation is followed by the change in pressure with time and by chemical analysis; and a 'continuous flow' method in which the reacting medium is passed at constant velocity through a uniformly heated tube, the progress of events being followed by analyses of samples taken at suitable intervals.

The vessels or tubes employed are usually of pyrex glass, transparent silica, or porcelain, and the experiments are carried out at atmospheric or reduced pressures.

Methane—Slow Combustion. At atmospheric pressure methane will react with oxygen at temperatures of about 420° C. and upwards, the products consisting of the two oxides of carbon and steam together with small quantities of formaldehyde and formic acid. The reaction is marked by a well-defined induction period followed by a period of relatively rapid reaction during which the pressure rises and the greater part of the hydrocarbon or oxygen (whichever is in defect) is used up. In Fig. 1 is shown a series of typical pressure-time curves for methane-oxygen mixtures of varying composition at a pressure of 760–70 mm. reacting in a silica vessel maintained at 447° C.; and in the accompanying table are the corresponding observed times of induction and reaction (Bone and Allum [7, 1932]).

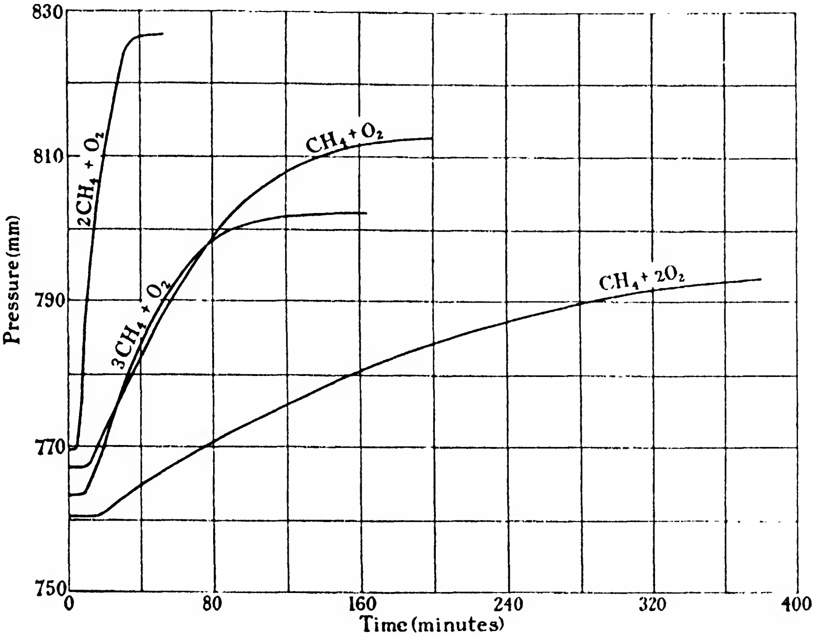


FIG. 1. Curves showing influence of mixture-composition on rate of reaction at 447° C. (*By courtesy of the Royal Society.*)

Original mixture	*Duration of observed periods of*		*Percentage of initial oxygen remaining at end of observed 'reaction' period*
	induction, min.	*reaction, min.*	
$3CH_4+O_2$	10	153	nil
$2CH_4+O_2$	4	36	nil
CH_4+O_2	12	1,507	2·3
$CH_4+1{\cdot}86O_2$	21	364	53·1

It may be noted that, whether judged by induction or reaction, the most reactive mixture is one containing methane and oxygen in the ratio 2 : 1. An inspection of the pressure-time curves indicates that there is an exponential growth of the rate of reaction with time during the early stages, the maximum velocity being attained approximately at the moment when half the oxygen has been consumed.

The effect of increase of initial pressure or reaction temperature is to shorten both the induction and reaction periods, as shown by the following figures relating to a $2CH_4+O_2$ mixture:

Influence of temperature at atmospheric pressure			*Influence of pressure at 447° C.*		
	Observed duration of			*Observed duration of*	
Temp. ° C.	*induction, min.*	*reaction, min.*	*Pressure, mm.*	*induction, min.*	*reaction, min.*
447	4	36	770	4	36
442	5	65	706	10	160
435	11	150	575	12	270
423	50	..	..	..	..

Comparative experiments with mixtures containing varying proportions of methane and oxygen show that the rate of reaction is determined by a power of the methane concentration between 2 and 3, and of the oxygen concentration between 1 and 2. The effect of increase of surface (as, for example, by filling the reaction vessel with silica tubes) is to retard the reaction, whilst the presence of traces of certain substances such as formaldehyde and methyl alcohol eliminates or shortens the induction period and speeds up the subsequent reaction.

Analytical Data showing the Full Course of the Slow Reaction.

The curves in Fig. 2 and the data in Table III relate to a $2CH_4+O_2$ mixture reacting at 447° C. and atmospheric pressure [7, 1932]. They show that following an induction period of 6 min., during which little or no reaction takes place, some 40 min. elapse before half the oxygen is consumed. At the end of the induction period the only detectable products are formaldehyde (0·17%) and steam. After 97 min. only 4·6% of free oxygen remains in the system and the reaction has become exceedingly slow. The carbon-hydrogen-oxygen balances show that all the carbon of the methane burnt (save the small amount present as formaldehyde) is accounted for as carbon monoxide and dioxide.

Combustion at Reduced Pressures. The influence of pressure and temperature upon the induction and reaction periods has already been referred to, and it was pointed out that if the reaction rate is increased beyond a certain limiting value heat will accumulate in the system and inflammation and explosion may result. By carrying out experiments at low pressures (15 cm. of mercury or less) it becomes possible to follow the progress of oxidation at much higher velocities. In these circumstances it is found that when an explosive mixture is admitted to a sufficiently hot enclosure there is a period of induction which, in the case of methane, may amount to an hour or more, followed by an abrupt inflammation. The induction period, as before, depends upon temperature and pressure increasing as one or both are progressively lowered until at some critical value inflammation will no longer occur.

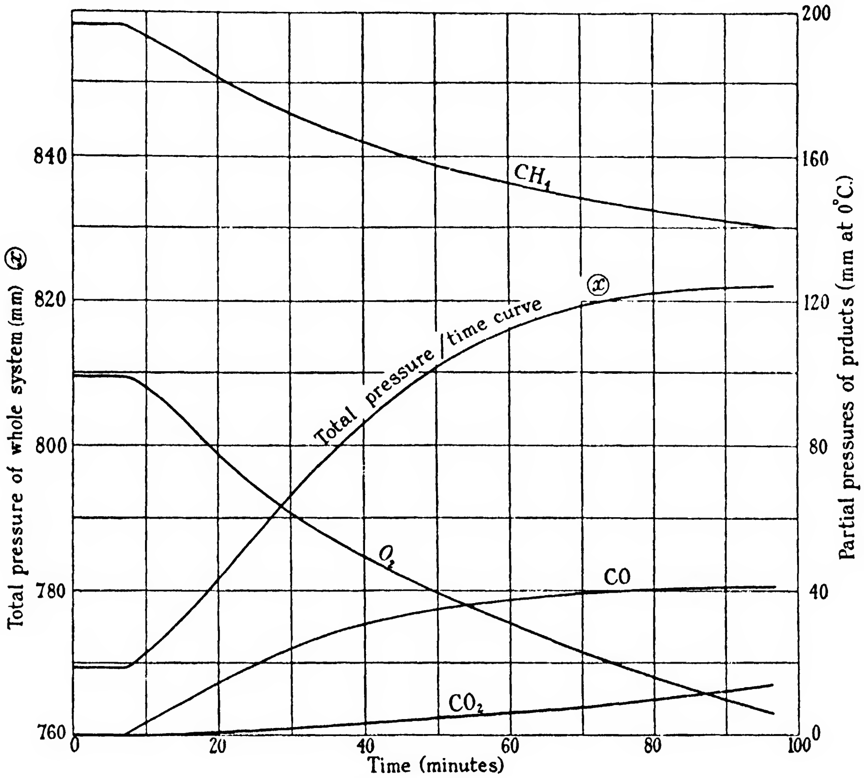


FIG. 2. Dry $2CH_4+O_2$ mixture at 447° C. (*By courtesy of the Royal Society.*)

TABLE III

Experiments with Dry $2CH_4+O_2$ *Mixture at* $T = 447°$ *C.* (*Bone and Allum*)

Time in minutes from start (induction period = 6 min.)	6			21			28			44			57			97		
Initial pressure of dry mixture at T° C.	mm. 761·4			mm. 769·6			mm. 758·1			mm. 760·5			mm. 750·6			mm. 762·2		
Final pressure of products at T° C.	761·4			779·6			775·4			793·1			799·4			822·3		
Partial pressure of original mixture at 0° C.:	mm.			mm.			mm.			mm.			mm.			mm.		
CH_4	196·5			199·5			197·0			197·5			197·4			196·8		
O_2	97·9			99·2			98·0			98·3			98·2			98·0		
Partial pressure of gaseous products (mm.) at 0° C.:																		
CO_2	nil			0·6			1·6			3·7			5·2			14·4		
CO	nil			18·1			17·7			32·7			35·8			40·6		
CH_4	196·0			179·0			176·7			161·0			155·8			141·3		
O_2	97·5			71·7			66·5			43·0			35·8			4·6		
C, H_2, O_2 balances	C	H_2	O_2	C	H_2	O_2	C	H_2	O_2	C	H_2	O_2	C	H_2	O_2	C	H_2	O_2
Units in original mixture	196·5	393·0	97·9	199·5	399	99·2	197·0	394·0	98·0	197·5	395	98·3	197·4	394·3	98·2	196·8	393·6	98·0
Units in products	196·0	392·0	97·5	197·7	358	81·3	196·0	353·4	77·0	197·4	322	63·0	196·8	311·6	58·9	196·3	282·6	39·3
Difference as H_2O (and traces of H·CHO)	0·5	1·0	0·4	1·8	41	17·9	1·0	40·6	21·0	0·1	73	35·3	0·6	82·7	39·3	0·5	111·0	58·7

According to Neumann and Egorow [41, 1932], the relation between pressure (p), absolute temperature (T), and induction period (t) for methane-oxygen mixtures is given by

$$k = p^{1\cdot 8}\, t e^{-41,000/T},$$

where k is a constant depending upon the ratio of the reacting gases and the dimensions of the vessel.

Neumann and Serbinoff [42, 1933] have also found that for certain methane-oxygen mixtures (containing 2·5–37% of methane) there are three pressure limits to explosion. Their results, illustrated by the curve in Fig. 3, show that at 640° C., for example, ignition will occur at pressures between 4 and 9 cm. of mercury and again above 34 cm., whilst between 9 and 34 cm. and below 4 cm. ignition will not take place. This sudden change from a slow to a self-accelerating reaction under nearly isothermal conditions is difficult to explain except by a 'branching chain' mechanism such as has been referred to earlier. Further examples of this phenomenon and a fuller discussion of its implications will be found in the article by the authors on 'Ignition' in the Detonation Section (Article 5).

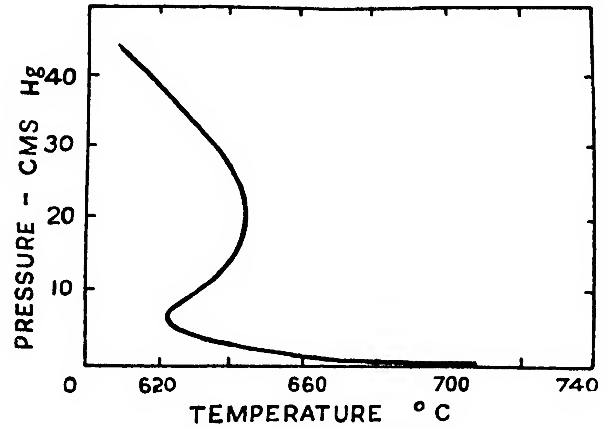


FIG. 3.

Slow Combustion at High Pressures. The characteristics of the high-pressure combustion of methane will be referred to in detail later; it will suffice to mention here that amongst the products of such combustion is methyl alcohol, in considerable quantities.

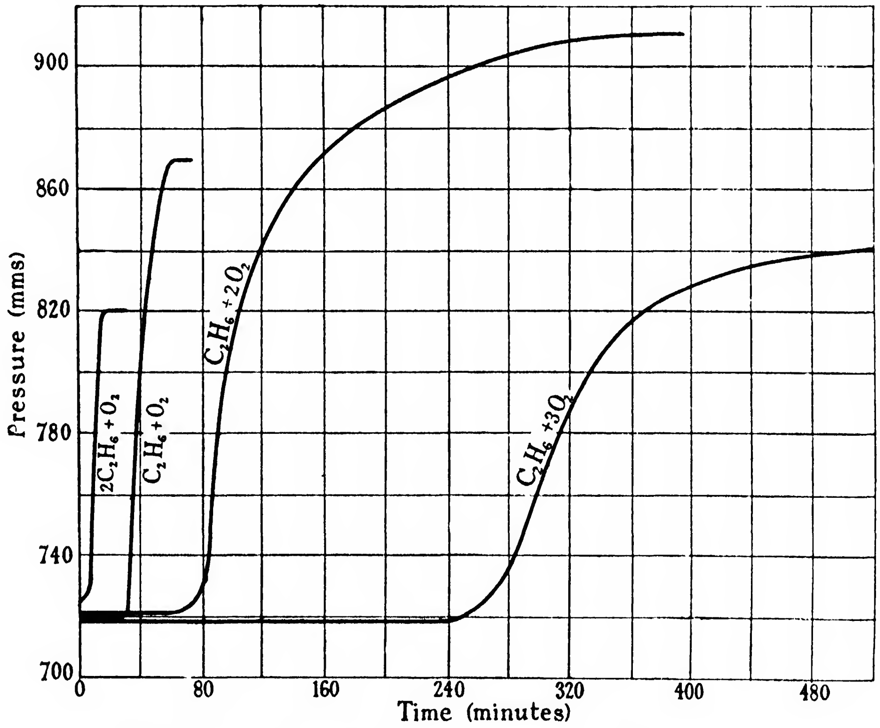


FIG. 4. Time-pressure curve at 316° C. (*By courtesy of the Royal Society.*)

Ethane. The Slow Combustion at Atmospheric Pressure. Ethane behaves in a similar manner to methane, the most reactive mixture being that containing ethane and oxygen in the ratio 2 : 1. The curves in Fig. 4 show the relation between pressure and time for mixtures of varying composition reacting in a silica vessel at atmospheric pressure and 316° C. [10, 1930].

The effect of small quantities of certain third bodies upon the induction and reaction periods is particularly well marked, as may be seen by the data in Table IV.

TABLE IV

Duration of Induction and Reaction Periods with a Dry $C_2H_6+O_2$ *Medium at 316° C. and 720–30 mm. with various Additions (Bone and Hill)*

	Induction, min.	*Reaction, min.*
Dry $C_2H_6+O_2$ . .	30	70
plus 1% moisture . .	10	25
plus 1% C_2H_5OH . .	6	18
plus 1% iodine . .	5	25
plus 1% NO_2 . .	0	20
plus 1% CH_2O . .	0	20
plus 1% CH_3CHO .	0	Immediate inflammation

It will be noted that these added compounds which eliminate the induction period are in all cases substances which on thermal decomposition or further oxidation followed by decomposition are able to liberate oxygen atoms.

The products of the slow combustion are acetaldehyde, formaldehyde, formic acid, a peroxide or peracid, the two oxides of carbon, and steam.

In the accompanying Fig. 5 and Table V are given data relating to the full course of the reaction of a $2C_2H_6+O_2$ mixture at 303–305° C. and 687–9 mm.

The more important points brought out by these experiments are (1) that during the 'induction' period of 15 min. only inconsiderable amounts of oxygen are consumed and no intermediate products are detectable, (2) that aldehydes and peroxides appear together, reach a maximum at about the point of maximum reaction velocity, and thereafter diminish, (3) there is no separation of carbon or liberation of hydrogen, and (4) the carbon-hydrogen-oxygen balance based upon the experimental data indicate that either C_2H_6O or some less oxygenated ethane is also present among the soluble and condensable products, and the fact that this compound tends to accumulate as the oxygen of the original mixture is used up suggests that it is a primary product of the oxidation.

The Slow Combustion at High Pressure. When an ethane-oxygen mixture containing an excess of the hydrocarbon reacts at pressures of 10 atm. or higher, there are found in the products, in addition to the substances already mentioned, considerable quantities of ethyl alcohol, methyl alcohol, and acetic acid [43, 1932]. On carrying out the oxidation by a continuous flow method in suchwise that the reacting medium is subjected to heat for a short period only and is immediately cooled, it is possible partially to arrest the oxidation so that the initial products are found in large quantities. Thus when a $C_2H_6 = 90$, $O_2 = 3$, $N_2 = 7\%$ mixture at 50 atm. pressure is passed through a tube heated to 360° C. at such a rate that the duration of heating is only 4 sec., the composition of the products expressed as percentages of the carbon of the ethane burnt is as follows: C_2H_5OH 62·6, CH_3CHO 4·8, $CH_3COOH = 1·1$, $CH_4 = 9·3$, CO 9·2, $CO_2 = 4·7\%$.

Ethylene. The products of the slow combustion are ethylene oxide, acetaldehyde, formaldehyde, a peroxide, formic acid, the two oxides of carbon and steam, whilst in special circumstances the presence of glyoxal and dioxy-methyl peroxide have been reported.

In Fig. 6 the pressure-time curves for ethylene-oxygen mixtures of varying proportions reacting in a silica vessel at atmospheric pressure and 300° C. show that the $2C_2H_4+O_2$ mixture is the most reactive, and that with all those originally containing more than the equimolecular proportion of ethylene there was a slight fall of pressure during the induction period and the subsequent pressure rise was also succeeded by a pressure fall. The duration of these changes are recorded in Table VI [9, 1933].

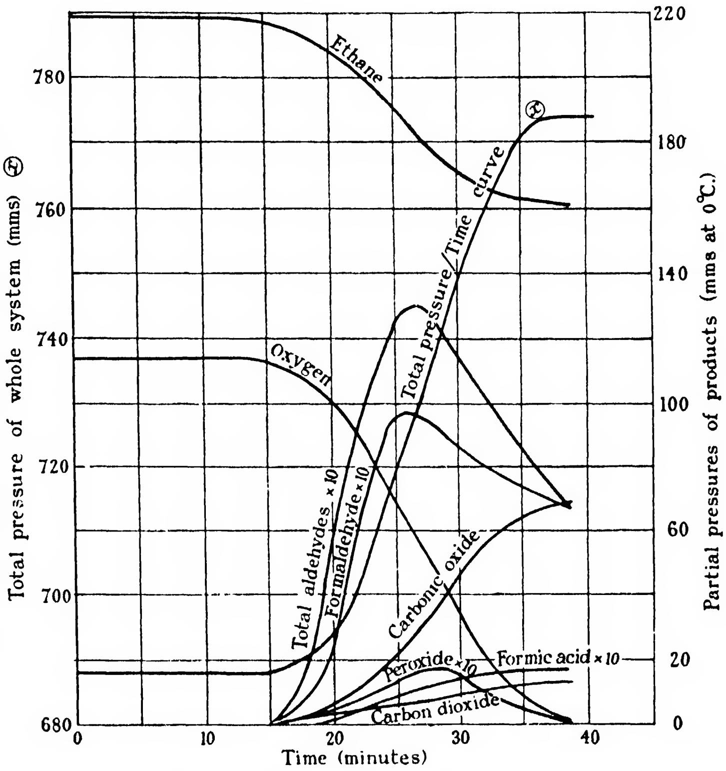


FIG. 5. $2C_2H_6+O_2$ at 303–305° C. (*By courtesy of the Royal Society.*)

A more detailed study of the kinetics point to the reaction being approximately third order, the rate depending more upon the concentration of the ethylene than of the oxygen [54, 1929]. The effect of the addition of small quantities of third substances upon the duration of induction and reaction periods of a $C_2H_4+O_2$ medium (P_2O_5-dried) at 300° C. and 760 mm. is set forth in Table VII. Attention may be drawn to the marked contrast between

TABLE V

Experiments with a $2C_2H_6+O_2$ *Mixture at* $T = 303–305°$ *C.* (*Bone and Hill*)

Time in minutes from start (induction period — 15 min.)	15			21·5			25			28·5			31·5			38		
Partial pressures (mm.) in original mixture at 0° C.:																		
C_2H_6	218·5			215·9			216·2			218·6			218·3			218·5		
O_2	114·0			112·6			112·8			114·1			113·9			114·0		
Partial pressures (mm.) of gaseous products at 0° C.:																		
CO_2	2·3			2·8			4·9			7·6			10·7			12·9		
CO	2·7			9·4			22·1			36·6			55·0			68·7		
C_2H_6	216·5			204·6			189·8			177·5			167·0			161·1		
O_2	111·0			93·7			69·2			48·4			21·3			1·3		
Partial pressures (mm.) of liquid products reduced to 0° C.:																		
CH_3CHO	nil			2·2			2·5			3·1			1·9			nil		
H·CHO	nil			6·0			9·5			9·1			7·9			6·7		
$C_2H_4O_2$	nil			0·3			1·3			1·8			0·9			nil		
H·COOH	nil			nil			0·9			1·3			1·6			1·7		
C, H_2, O_2 balance	C	H_2	O_2	C	H_2	O_2	C	H_2	O_2	C	H_2	O_2	C	H_2	O_2	C	H_2	O_2
Units in original mixture	437	655	114	432	648	113	432	649	113	437	656	114	437	655	114	437	656	114
Units in above products	438	650	114	432	625	106	424	588	94	420	553	84	415	516	67	412	492	54
Difference = Units as H_2O and 'oxy-C_2H_6'	..	..	..	0	23	7	8	61	19	17	103	30	22	139	47	25	164	60

the effects of additions of the two isomers, acetaldehyde and ethylene oxide.

The data for the progressive reaction of a $2C_2H_4+O_2$ medium at 300° C. are recorded in full in Table VIII and are shown graphically for all stages of the reaction in Fig. 7.

It should be noted that (1) the carbon-hydrogen-oxygen balance indicates the presence of C_2H_4O isomers, accumulating as the oxygen in the system approaches exhaustion, (2) formaldehyde and formic acid both reach a maximum in the system some time before the pressure rise ends, and (3) that peroxide formation follows upon a certain accumulation of formaldehyde, reaches a maximum before the

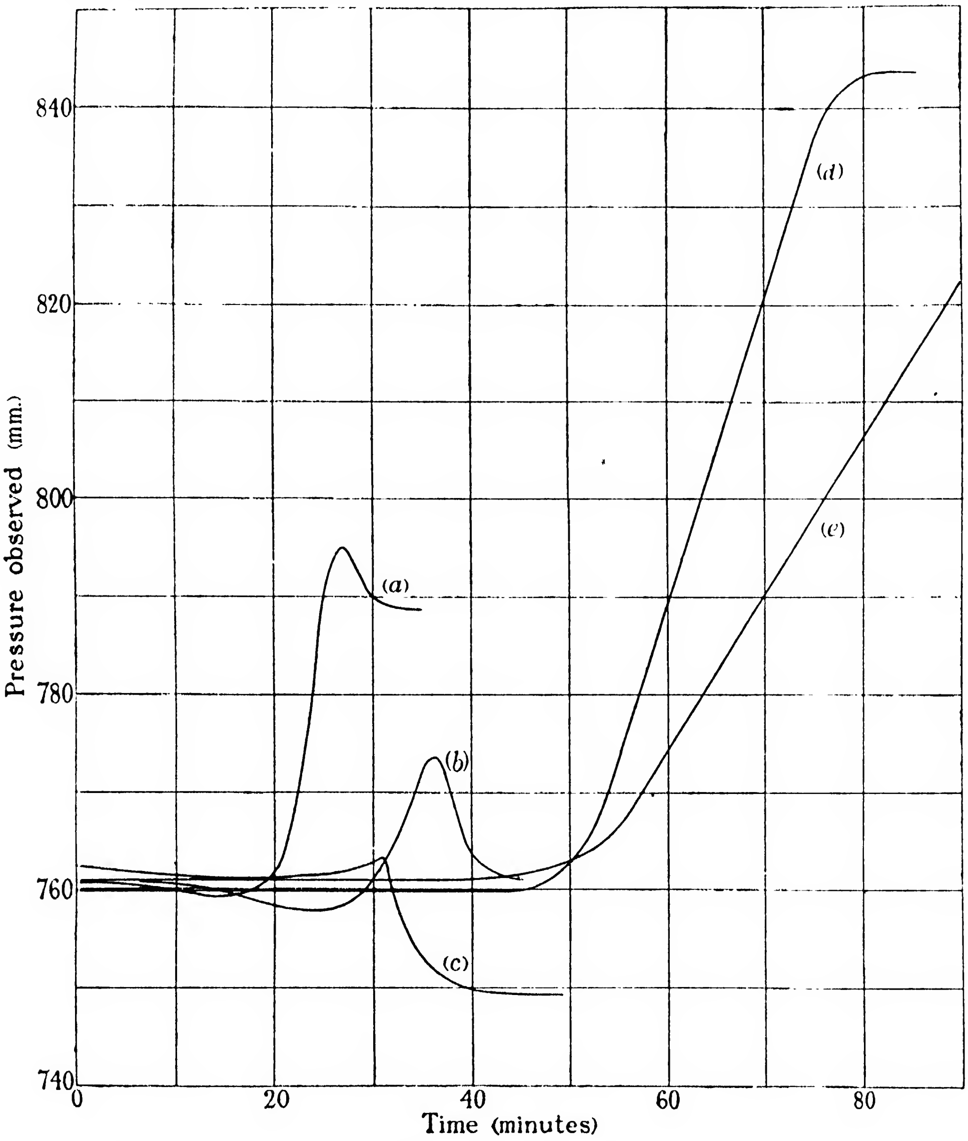


FIG. 6. Observed pressure-time curves with various C_2H_4-O_2 mixtures. (*a*) $2C_2H_4+O_2$ (3); (*b*) $3C_2H_4+O_2$ (2); (c) $5C_2H_4+O_2$ (1); (*d*) $C_2H_4+O_2$ (4); (*e*) $C_2H_4+2O_2$ (5). The numbers in brackets correspond to the numbers in Table III. (*By courtesy of the Royal Society.*)

TABLE VI

Induction and Reaction Periods of Ethylene-Oxygen Mixtures reacting at Atmospheric Pressure and 300° C. (Bone, Haffner, and Rance)

	Duration in minutes of			
		Reaction		
Mixture	*Induction*	*Pressure rise*	*Pressure fall*	*Total*
$5C_2H_4+O_2$	24	7	13	20
$3C_2H_4+O_2$	25	11	9	20
$2C_2H_4+O_2$	16	11	5	16
$C_2H_4+O_2$	44	36	0	36
$C_2H_4+2O_2$	47	330+	0	330+

TABLE VII

	Duration in minutes of			
		Reaction		
$C_2H_4+O_2$	*Induction*	*Pressure rise*	*Pressure fall*	*Total*
P_2O_5 dried	54	37	13	50
plus 1% H_2O	56	29	21	50
1% NO	0	20	8	28
1% CH_3CHO	2	42	8	50
1% ethylene oxide	45	75	10	85
1% HCHO	25	38	13	51

latter, and disappears some time before all the oxygen has been used up. The pressure fall towards the close of the reaction when presumably the primary product of the oxidation would be accumulating suggests that the formation of the latter involves a reduction in volume. Mention may be made of a series of experiments carried out by Blair and Wheeler [5, 1922–3] with ethylene-oxygen-nitrogen mixtures with special reference to the production of formaldehyde. A circulation method was employed, the reaction tube being of hard glass 3–4 mm. in diameter.

TABLE VIII

Data for a $2C_2H_4+O_2$ *Reaction at* $T = 300°$ *C.*

Duration in minutes of—			
Induction	16		
Reaction: Pressure rise	11	16	
Reaction: Pressure fall	5		
Partial pressures (mm.) in original mixture at 0° C.:			
C_2H_4	240		
O_2	114		
Partial pressure (mm.) of measured products at 0° C.:			
C_2H_4	153·0		
O_2	0·0		
CO_2	13·6		
CO	79·0		
C_nH_{2n+2}*	4·3		
H·CHO	16·0		
H·COOH	3·0		
Peroxide	nil		
C, H_2, O_2 balance	C	H_2	O_2
Units in original mixture	480	480	114
Units in measured products	426	338	64
Differences	54	142	50
Calculated as C_2H_4O	54	54	13
Leaving as water	..	88	37

* C_nH_{2n+2} = mixture of ethane and propane.

The following is a summary of some of their results:

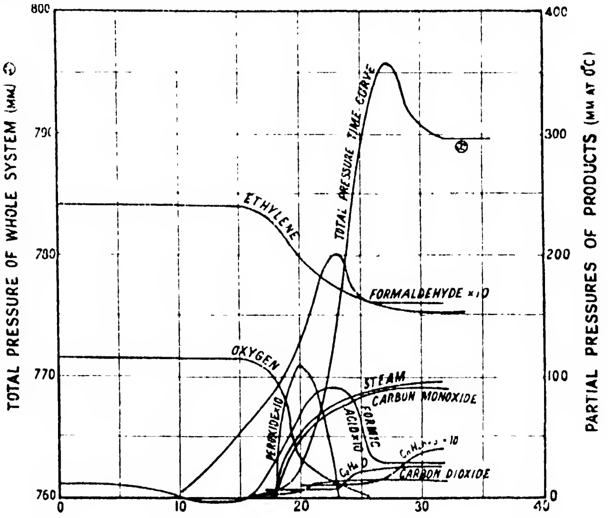
Temp. of expt.	*% C_2H_4 in mixture before and after expt.*	*% of oxygen in mixture before and after expt.*	*Rate of passage of gas*	*% of C_2H_4 converted to* HCHO
			c.c. per min.	
560	15·1–10·8	9·6– 3·5	30	50
575	13·4–10·5	14·9–13·0	50	70
600*	14·9–17·5	11·6– 0·0	31	1·5

* A steel tube was used in this experiment.

Also, under conditions of very slow reaction at 560° and with a large excess of oxygen, as much as 51·1% of the ethylene burnt was recovered as acetaldehyde and a further 28·9% as formaldehyde. These results are of particular interest as showing that the oxidation may be almost completely arrested at an early stage.

Acetylene. The slow combustion of acetylene has been studied by static, circulation, and continuous flow methods.

When acetylene-oxygen mixtures are heated in a closed glass vessel interaction begins at about 250° C. and proceeds rapidly at 300° C. In the case of a mixture corresponding to $2C_2H_2+O_2$ and $C_2H_2+O_2$ explosive combustion sets in at 350° C. and with mixtures corresponding to $2C_2H_2+3O_2$ at 375° C. The rate of combustion is retarded and the ignition point is always raised by either reducing the initial pressure or by the addition of oxygen over and above an equimolecular proportion. Analyses show that carbon monoxide and formaldehyde simultaneously arise at an early stage of the process, probably as the result of the decomposition of an unstable initial product $C_2H_2O_2$. Formic acid, carbon dioxide, and steam together with traces of acetaldehyde are also found in the products, and the presence of glyoxal has been reported in continuous flow and circulation experiments [11, 1927].



TIME (MINUTES)

FIG. 7.

Reference may be made to some experiments by Spence and Kistiakowsky [53, 1930] in which acetylene-oxygen mixtures were circulated through a pyrex glass tube heated to a temperature of about 320 C. and the progress of the reaction followed by the change of pressure in the system and by chemical analysis.

It was found that reaction was preceded by an induction period and that the rate of reaction was accelerated by oxygen when acetylene was in excess, but was slightly retarded by it when oxygen was present in excess. At the optimum oxygen concentration the rate was proportional to the square of the acetylene concentration.

The products consisted of glyoxal, formaldehyde, formic acid, the two oxides of carbon, and steam. No free hydrogen was found and no carbon was deposited.

The following balance calculated from the analysis of the products from a mixture of composition C_2H_2=357·0 mm., O_2 = 129·0 mm. reacting at 320° C., shows the distribution of the original carbon in the products:

Product	*G. atoms of carbon* × 10^3
$C_2H_2O_2$	0·783
HCHO	0·545
H·COOH	0·376
C_2H_2	19·180
CO_2	0·182
CO	2·798
Total	23·864
In initial gases	23·960

In reviewing their results Spence and Kistiakowsky consider that the induction period is caused by a gradual accumulation of some condensable substance which is necessary for the reaction to acquire its full rate and suggest that it can be identified as one or all of the three condensable products, glyoxal, formaldehyde, and formic acid. Attention is also drawn to the fact that during the reaction formaldehyde is oxidized to formic acid at temperatures at which it would not normally be attacked. Taking these facts into consideration, they conclude that oxidation proceeds by a chain mechanism but that there is insufficient evidence to specify it in detail.

The Slow Combustion of the Higher Hydrocarbons.

In dealing with the higher hydrocarbons a much greater degree of complexity in the combustion must be expected due to the increased number of intermediate stages and the probability of secondary reactions interfering with the main course of events. The data necessary for defining accurately the changes that occur is still far from complete; no full analyses of the products are available, and the evidence for deciding the point of initial attack of oxygen on the hydrocarbon molecule is not conclusive.

Generally speaking, combustion appears to have the characteristics associated with a chain mechanism (cf. oxidation of pentane, Pidgeon and Egerton [20, 1932]); there are well-defined induction periods and the rates of reaction are retarded by increasing the surface-volume ratio of the containing vessel. The most reactive mixtures are the 2:1 or 1:1 (hydrocarbon-oxygen) and, as with the lower members, the rates are increased by increase in the hydrocarbon concentration and are unaffected or retarded by increase in the oxygen.

A phenomenon of considerable significance is the occurrence of well-defined zones of luminosity during the slow combustion; this effect is most pronounced with the higher hydrocarbons, but also occurs to some extent with those of low molecular weight. Its nature may best be understood by describing what takes place in a particular instance. Only brief reference is made to the phenomenon, as the subject is dealt with again in the section on Detonation.

When a pentane-air mixture containing less than the theoretical quantity of the hydrocarbon for complete combustion is passed through a pyrex glass tube at the rate of 5 litres per hour and the temperature of the tube slowly increased from 20 to 700° C., nothing is visible until about 240° C. At this temperature (θ_1) a feeble luminosity is apparent, increasing in intensity until about 300–350° C.; as the temperature further increases, the luminosity is masked by the red-hot walls of the tube (from 525–550° C. upwards). Ignition occurs at 660–670° C., the flame being of a blue colour and appearing intermittently at the entrance to the tube (vide Prettre [51, 1931] and Article 4 in Section 42 of this work).

For mixtures containing more than the theoretical quantity of pentane different phenomena occur. Luminosity is first observable at about 220° C. (θ_1) and remains fairly constant in intensity up to about 240° C. (θ_2); the intensity then increases rapidly, especially near the exit of the tube, until at about 260° C. (t_1 = temperature of first inflammation) a brilliant sharp flame appears at the exit end and travels slowly towards the inlet. As the temperature rises, a succession of similar flames appear, travel to the inlet, and are extinguished; it is observable that with increasing temperature they become more diffuse in outline and travel slower until at 290° C. (t_2) flame is no longer formed, although luminosity varying in intensity still persists. Above 350° C. the luminosity becomes uniform and remains so until it is masked by the red-hot walls of the tube. Between 670 and 710° C. (T = temperature of second inflammation) ignition occurs at the inlet end of the tube, the flame showing pulsations.

The data in the accompanying table relate to a series of experiments with pentane-air mixtures of varying strengths.

TABLE IX (*Prettre*)

Pentane content %	*Rate of flow, litres per hour*	θ_1° *C.*	θ_2° *C.*	t_1° *C.*	t_2° *C.*	*T*° *C.*
1·3	5·70	250	..	..	..	680
2·1	3·00	242	..	..	..	670
2·35	4·30	230	..	..	..	660
2·60	5·40	225	237	263	285	672
4·05	6·50	221	240	262	292	681
6·15	5·80	225	235	261	286	710
16·55	4·80	225	244	259	270	Beyond limit

All the flames formed between 260 and 290° C. in excess pentane-air mixtures originate at the exit end of the tube. This seems to show that ignition at these temperatures is possible only by the formation of some intermediate product whose combustion induces flame; it is not the intermediate product only that burns, because the flame once formed travels backwards to the inlet end of the tube, where, presumably, such product would be absent. It should be noted that the temperature T is higher than the true ignition temperature, probably owing to some dilution of the initial mixture with the product of combustion. Chemical analyses show that between 100 and 220° C. traces of aldehyde are present in the products; as luminosity appears the aldehyde content increases parallel with its intensity until when the first flame is formed one bubble of gas from the exit end of the tube produces a deep colour with Schiff's reagent. When the temperature exceeds θ_1, dense vapours appear which condense to give an oily liquid of acid reaction.

Propane, hexane, heptane, and octane behave in a similar manner to pentane. Ethane, on the other hand, becomes luminous at 350–400° C., but does not inflame below 650° C., whilst methane only shows luminosity in the neighbourhood of its ignition temperature 720–780° C.

Of the olefines ethylene shows luminosity at 420° C. and inflames at 600° C., whilst amylene behaves much like the higher paraffins.

Another interesting fact that has recently been discovered in connexion with the higher hydrocarbons is the existence under certain circumstances of a negative temperature coefficient. This was first observed by Pease and Munro [48, 1929; 49, 1934] in the case of propane-oxygen-nitrogen mixtures undergoing slow combustion in a continuous flow system, and has since been confirmed by other workers. Pease and Munro found that when a propane = 1, oxygen = 1, nitrogen = 2 mixture was passed through a heated pyrex glass tube, combination took place readily at 350° C. but not at 300, 400, or 450° C. At 475° C. the mixture became mildly explosive. The reaction rate first increased with temperature between 300 and 350° C., then decreased to zero as the temperature was raised to 450° C., after which it again increased. When the nitrogen content of the mixture was increased to 75% the whole of the low-temperature reaction was suppressed and only the high-temperature reaction (500–600° C.) with its positive temperature coefficient but without its explosive character remained.

So important is this phenomenon on its bearing upon internal-combustion engine theory that we propose to give an account of another investigation by Beatty and Edgar with *n*-heptane-air mixtures, which throws further light on the matter [2, 1934]. The method employed was to vaporize *n*-heptane in nitrogen and add oxygen in proportions such that the ratio of the two gases was the same as in air, and the oxygen/fuel ratio was approximately the theoretical for complete combustion (i.e. 1·9% of fuel vapour). The preheated mixture was then passed at constant rate (so as to give a time of contact in the reaction tube of 40 sec. at 200° C.) through a pyrex glass tube of 2·41 cm. diameter and 65 cm. long. The amount of reaction was determined by measurements of (1) the oxygen consumed per mol. of fuel input, and (2) the percentage of fuel input which was oxidized.

It was found that slow oxidation could first be detected at about 150° C. and that at 217° C. 9·0 mol. of oxygen were used for every mol. of fuel oxidized (theoretical 11 mol.). The absence of an induction period and the large oxygen consumption suggest a heterogeneous reaction resulting in nearly complete combustion of each fuel molecule that is attacked.

At about 250° C. the percentage of heptane oxidized increased rapidly, and at 270° C. 70·5% was oxidized, of which 24% disappeared in the first 5 cm. length of the reaction tube. The oxidation at this stage was definitely of the homogeneous chain-reaction type and was accompanied by visible chemi-luminescence. At the same time the oxygen consumption decreased to 3·0 mol. per mol. of fuel oxidized. At about 270° C. a mild explosion occurred causing pulsation of the flow meter in the system and visible flame-like movements in the luminescent gas; these ignitions, at first 8 or 10 sec. apart, occurred more rapidly as the temperature was raised, until at about 305° C. they became continuous. At this stage marked local evolution of heat became apparent, with the result that the maximum temperature of the gas rose abruptly to 350° C.; the reaction velocity increased rapidly, but the amount of oxidation remained constant at 3 mol., and only 81% of the heptane was oxidized (at 340° C.). This phase of the combustion is called by Beatty and Edgar the 'primary' reaction.

Continuing up the temperature scale there was a sharp increase in the total amount of oxidation (from 3·0 to 4·7 mol. of oxygen) from 350 to 380° C. due, it was considered, to a subsequent reaction. From 380 to 490° C. no change whatever in the total amount of oxidation took place, although the oxygen used was only 42·7% of the theoretical for complete combustion. This extraordinary passivity implies an unexpectedly high stability of the reaction products with respect to oxygen. Finally, at the inflammation point (about 525° C.) the mixture ignited at a point some 15 cm. from the inlet, a rapid, greenish-blue flame moving in both directions at intervals of 5 sec. At this stage complete combustion to carbon dioxide and steam took place. With further increase of temperature the inflammation became continuous and occurred at the inlet to the tube.

With regard to the products of combustion, carbon dioxide appeared first and increased steadily to 0·75 mol. per mol. of fuel input at 380° C., which amount then remained constant up to the inflammation point. On the other hand, the amount of carbon monoxide formed increased with the oxygen consumption in a step-wise manner and reached 2·15 mol. at 380°; it then rose slowly but steadily with further increase in temperature, attaining a value of 3·0 mol. at 470° C. Finally, at some indefinite temperature between 500 and 525° C. inflammation occurred with complete combustion to carbon dioxide and steam.

Although the amount of reaction from 380 to 490° C. remained constant, the rate underwent a remarkable change. From 380 to 490° C. the temperature coefficient of velocity was markedly negative, the percentage of reaction completed in the first 25 cm. of the reaction tube falling from 93 to 75, and in the first 5 cm. from 88·3 to 62·1.

The change in luminosity and the negative temperature coefficient point unmistakably to the occurrence of successive stages in the oxidation; both effects, moreover, are closely associated with change in the spontaneous ignition temperature of the hydrocarbon, and reference should be made to the articles in the Detonation section entitled 'Ignition in Gases with Special Reference to Knock Problems' for a further discussion of their significance.

The Point of Initial Oxygen Attack. A number of investigations have been made with a view to ascertaining at what point a long chain hydrocarbon molecule is most open to attack by oxygen. The trend of the evidence so far obtained is in favour of oxidation first taking place at the end of the chain, although some isolated observations suggest that in certain cases the initial attack may be at a point farthest removed from a methyl group. Support for the former view is found in the work of Pope, Dykstra, and Edgar [50, 1929], who have compared the behaviour of *n*-octane undergoing slow combustion in air with that of the following five isomeric octanes:

$CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_3$	*n*-octane
$CH_3 \cdot CH_2 \cdot CH(CH_3) \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_3$	3-methyl heptane
$CH_3 \cdot CH_2 \cdot C(C_2H_5)_2 \cdot CH_2 \cdot CH_2 \cdot CH_3$	3-ethyl hexane
$CH_3 \cdot CH(CH_3) \cdot CH(C_2H_5) \cdot CH_2 \cdot CH_3$	2-methyl 3-ethyl pentane
$CH_3 \cdot CH(CH_3) \cdot CH_2 \cdot CH_2 \cdot CH(CH_3) \cdot CH_3$	2,5-dimethyl hexane
$CH_3 \cdot C(CH_3)_2 \cdot CH_2 \cdot CH(CH_3) \cdot CH_3$	2,2,4-trimethyl pentane

Their experimental method consisted in passing the preheated vapour-air mixture in the theoretical proportions for complete combustion through a 1-in. diameter pyrex glass tube, 3 ft. long, heated in an electric furnace. Experiments were carried out (*a*) at constant furnace temperature and (*b*) with slowly rising temperature (about 4° C. per min.), and the progress of the reaction was followed by analyses of samples of the gaseous products and by tests carried out on the liquid products.

In experiments with slowly rising temperature the combustion of *n*-octane could be divided into three temperature zones: 200–270, 270–650, and above 650° C. Below 200° C. no oxygen was consumed, but between 200 and 270° C. the oxygen content of the medium decreased regularly until the consumption calculated per mol. of octane oxidized amounted to about 2 mol. The liquid products consisted mainly of aldehyde and water and the gaseous products of carbon dioxide. Carbon monoxide was practically absent until just below 270° C., and hydrogen and methane were never detected. There was, however, a small amount of some gas absorbed by fuming sulphuric acid, the nature of which was not determined. The quantities of the oxides of carbon present at the different temperatures are shown by the curves in Fig. 8.

At about 270° C. some change in the reaction was indicated by the occurrence of a feeble luminescence which appeared to move counter-current to the gas flow and by pressure pulsations in the reacting medium. At the same time there was a sudden increase in the carbon monoxide content of the products. With rising temperature the pressure pulsation gradually diminished and at 300–320° C. were no longer noticeable—whilst the carbon monoxide content had risen to 1 mol. per mol. of octane consumed. Above 350° C. the oxygen consumption increased gradually up to 650° C., where it was nearly 6 mol. per mol. of fuel oxidized. The carbon dioxide in the products increased up to 400° C., after which it remained constant until 650° C., when it again showed an increase—the carbon monoxide at the same time diminishing. At about 650° C. the luminescence gave place to a blue flame which moved with the gas stream but ultimately, at some higher temperature, settled at the outlet, combustion then being complete.

Parallel experiments with heptaldehyde and butyraldehyde showed essentially the same features. Pope, Dykstra, and Edgar consider that the early appearance of aldehyde and water, the invariable presence of considerable amounts of aldehyde under all conditions, and the general similarity between the oxidation curve of *n*-octane and of heptaldehyde indicate that the primary oxidation products of octane are heptaldehyde and steam, thus:

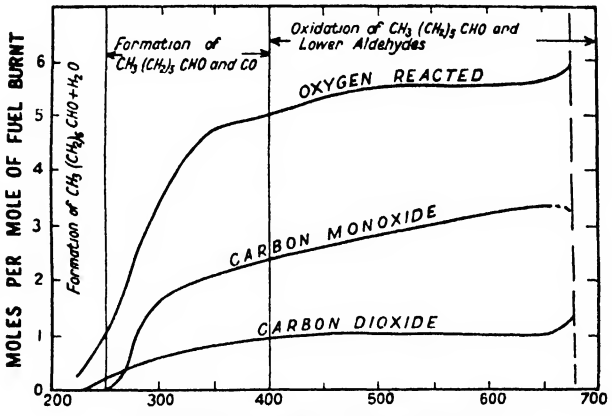


FIG. 8.

$$CH_3(CH_2)_6CH_3+O_2 \rightarrow CH_3(CH_2)_6CHO+H_2O,$$

the initial oxidation occurring at the end of the chain. The aldehyde first formed is then further oxidized to an aldehyde of lower molecular weight by one of the following reactions:

Main reaction

$$CH_3(CH_2)_6CHO+O_2 \rightarrow CH_3(CH_2)_5CHO+H_2O+CO$$

Side reaction

$$CH_3(CH_2)_6CHO+1{\cdot}5O_2 \rightarrow CH_3(CH_2)_5CHO+H_2O+CO_2$$

A detailed comparison of the results of the experiments with *n*-octane and heptaldehyde lend support to this view. Furthermore, it may be pointed out that with *n*-octane there is a distinct difference in the nature of the reactions giving rise to carbon monoxide and carbon dioxide. The latter is unaffected by the rate of heating and does not become an important factor until above 650° C. The reaction involving carbon monoxide appears at 270° C., shows a sharp decrease in its temperature coefficient at a slightly higher temperature, and is accompanied by pressure surges and luminescent flashes. No evidence was obtained of the formation of alcohols or of other than traces of peroxydic compounds.

The results of the oxidation of the five isomeric octanes may now be briefly summarized.

It is found that the point of initial attack is always at a methyl group rather than at a secondary or tertiary atom, and that hydrocarbons containing secondary or tertiary atoms are more resistant to oxidation than those without them. With the exception of 2,2,4-trimethyl pentane the remaining isomers behave generally in a similar manner to *n*-octane. The oxygen consumption curves, for example, show that an abrupt rise takes place below 300° C. followed by a period of slow rise as the temperature is further increased. The amount of oxygen used during the rise is found to correspond in the case of 2,5-dimethyl hexane to the oxidation of 1 carbon atom, and for 2-methyl, 3-ethyl pentane, 3-ethyl hexane, and 3-methyl heptane to the oxidation of 2, 3, and more than 3 carbon atoms respectively.

These results lead to the conclusion that in all cases but one oxygen attacks the methyl group at the end of the longest open-end straight chain of the hydrocarbon molecule forming an aldehyde and water; the aldehyde is then further oxidized with the formation of an aldehyde containing one less carbon atom, water, and one or other of the oxides of carbon. This reaction proceeds until a branch in the hydrocarbon chain occurs, when a ketone is formed which is more resistant to oxidation than are the aldehydes.

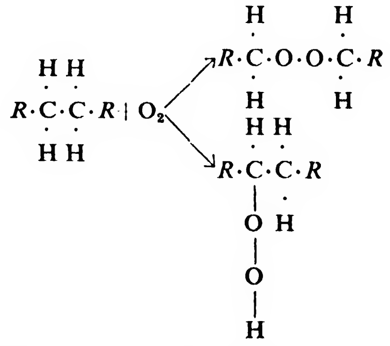
2,2,4-trimethylpentane has an open-end straight chain of only one carbon atom and possesses a highly condensed structure which renders it resistant to oxidation. It does not react until a temperature of about 500° C. is reached, when combustion proceeds at once to completion.

The alternative view that oxygen initially attacks the hydrocarbon molecule at a point farthest removed from a methyl group was suggested by Grün to explain the fact that the oxidation of liquid hydrocarbons in certain circumstances proceeds with explosive violence. He assumes that by a preliminary partial 'cracking' of the molecule a 'nascent' ethylene linkage is formed which offers a point of attachment for the oxygen; the initial product of the oxidation would then be an unstable alkyl peroxide.

The occurrence of acryl and propyl derivatives in the products of hexane oxidation would be satisfactorily explained on the above assumption; on the other hand, valeraldehyde and butyraldehyde have also been identified amongst the products and unquestionably arise from terminal oxidations. The experiments of Egerton and Pidgeon on the absorption spectra of burning hydrocarbons may be referred to in this connexion, for if appreciable quantity of ethylenic substances were formed by a preliminary partial cracking, such would give rise to sharp absorption, but no such absorption was observed (see Detonation section, Article 1).

The Formation of Peroxides.

Peroxides have frequently been detected during the oxidation of hydrocarbons, and the suggestion has been put forward that they are initially formed by the direct incorporation of oxygen in the hydrocarbon molecule, thus:



Their subsequent decomposition would then give rise to aldehyde and water [36, 1930–3].

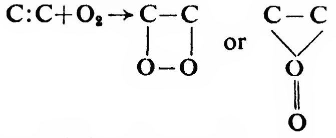
Peroxydic bodies, including alkyl peroxides, peracids, and hydrogen peroxide, are undoubtedly formed during slow combustion, and the presence of one or other has been reported by Callendar, Bone, Egerton, Lenher, Pease, and others in the products from both paraffin and olefine oxidations. The evidence available, however, is seldom sufficient to allow of the particular peroxydic body being identified, and no known alkyl or alkyl hydrogen peroxide has so far been isolated in such experiments.

One of the most convincing pieces of evidence of the formation of alkyl peroxide is to be found in the work of Dumanois, Mondain-Monval, and Quanquin [19, 1930]. These investigators employed hexane, heptane, and octane-air mixtures in a flow system in which the temperature of the reaction tube was slowly raised and observations made as to the nature of the gaseous and condensable products. With rise of temperature it was found that at about 200° C. there was a slight formation of aldehyde and carbon dioxide, whilst at 325° C. the reaction tube filled with heavy white fumes having a strongly aldehydic reaction, and there was an evolution of heat causing a temperature rise of some 40° C. The white fumes on condensation gave a liquid which separated into two layers, the lighter having a characteristic smell and containing besides some unchanged hydrocarbon, a considerable amount of formaldehyde, and small quantities of acet- and butyraldehyde. The aqueous lower layer was yellowish brown and had a strongly acid reaction; by rectification *in vacuo* a yellowish oil was obtained which possessed all the characteristics of an alkyl peroxide. With potassium iodide, for example, a violent reaction took place accompanied by evolution of hydrogen and liberation of iodine. Whilst with caustic potash considerable evolution of heat took place, hydrogen and a hydrocarbon were liberated, and the residual solution was found to contain formates and methyl alcohol. On heating the oil alone decomposition occurred at 200° C. with the formation of a 'cold' flame and liberation of aldehydes.

In the slow combustion of ethane Bone and Hill have shown that peroxides are only found in association with acetaldehyde, a circumstance suggesting that they, at any rate, partly arise from the oxidation of the aldehyde. Further evidence supporting this view is found in experiments by Newitt and Szego [45, 1934] on the pressure oxidation of ethane and acetaldehyde, and in the work of Bowen and Tietz [12] on the formation of peracetic acid and diacetyl-peroxide during the oxidation of acetaldehyde. Pease and Munro [49, 1934], on the other hand, found that peroxides, as distinct from peracids, were formed during the slow oxidation of propane in a flow system. Thus, on passing a 1:3 propane-oxygen mixture at 400° C. through a pyrex glass tube at the rate of 100 c.c. per minute, the ratio of peroxide to aldehyde in the products was 9 : 1. On coating the reaction tube with potassium chloride, however, the formation of peroxides was almost completely inhibited without greatly altering the total amount of reaction, a result suggesting that they are not essential to the propagation of the reaction.

The Slow Combustion of the Higher Olefines.

It might be expected that in the case of the olefines oxygen would be directly incorporated in the molecule at the double bond as follows:



$$C{:}C+O_2 \rightarrow \begin{array}{c} C-C \\ |\quad\; | \\ O-O \end{array} \quad \text{or} \quad \begin{array}{c} C-C \\ \diagdown\;\diagup \\ O \\ \| \\ O \end{array}$$

the initial product being a peroxide.

Experimental evidence, however, shows that the characteristics of such oxidations are similar to those of the paraffins and that the oxygen first attacks the end of the chain. Beatty and Edgar [3, 1934] have, for example, compared the behaviour of 1-heptene and 3-heptene with *n*-heptane undergoing reaction with the theoretical quantity of air for complete combustion in a flow system. Their results are shown graphically in Fig. 9.

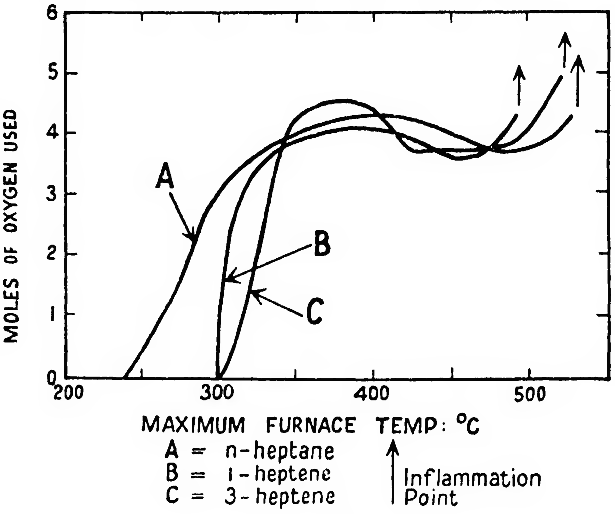


FIG. 9.

It was found that whilst with heptane oxidation began at 244° C., the heptenes did not react until the temperature had risen to 300° C. In all three cases the oxygen consumption increased rapidly between 350 and 400° C. to a maximum value which, however, was only about 40% of the theoretical for complete combustion. At about 400° C. the oxygen consumption showed a diminution due to the negative temperature coefficient of the reaction velocity, but with further rise of temperature the consumption again increased until between 500 and 550° C. combustion was complete. A more precise determination of the relative rates of reaction showed that at both low and high temperature there was a decided increase in velocity in going from 3-heptene to 1-heptene and thence to *n*-heptane.

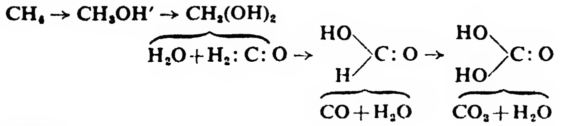
The Course and Mechanism of Hydrocarbon Combustion.

It will be opportune at this stage to consider briefly the more important theories of hydrocarbon combustion, pointing out the extent to which they are able to account for the experimental results recorded in the preceding pages. The oldest of these theories, the hydroxylation theory, was suggested by H. E. Armstrong as long ago as 1874 and was developed in its present form by W. A. Bone as the result of a series of researches extending over the period 1898–1902 [11, 1927]. ,

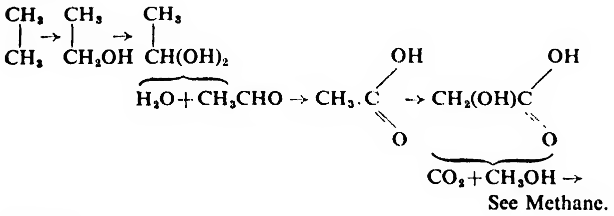
The Hydroxylation Theory is able to give an account of the course of combustion from slow reaction to explosion and detonation, and defines the nature of the intermediate products and the order in which they are formed. It is based largely upon the results of chemical analysis and does not postulate the intervention of any compound, capable of independent existence, which cannot be isolated and identified amongst the products of combustion.

According to the theory, the slow oxidation of a hydrocarbon involves a succession of hydroxylations and thermal decompositions mainly as follows:

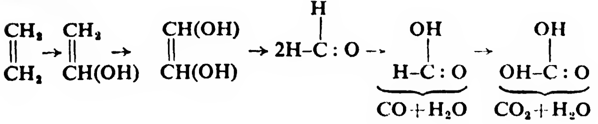
Methane



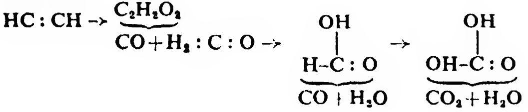
Ethane



Ethylene



Acetylene



It should be noted that, save in the case of acetylene, the initial product of the oxidation is always an alcohol; the second stage involves the transient formation of an unstable dihydroxy-derivative followed by its decomposition to water and an aldehyde; the third stage the conversion of the aldehyde either into a lower aldehyde or into the corresponding fatty acid; and finally, the further hydroxylation of the fatty acid and the subsequent breakdown of the dihydroxy compound so produced. Secondary reactions arising from thermal decompositions, condensations, or interactions of the intermediates may give rise to a variety of substances, including lower hydrocarbons, peracids, free carbon, and hydrogen.

Considerable interest attaches to the initial stage of the oxidation, which according to the theory is the formation of an alcohol. The analytical data shows that an alcohol is an important product of the combustion and also suggests that it precedes the formation of aldehyde; thus, for example, it will be recalled that, during the oxidation of methane at high pressure, alcohol tended to accumulate in the products as reaction approached completion, whilst during the oxidation of ethane at high pressure in a flow system no less than 82·6% of the carbon of the ethane burnt survived as ethyl alcohol and only 4·8% as acetaldehyde. Alcohol is not easy to identify amongst the products of combustion at ordinary pressure owing to the fact that it can oxidize more readily than does the parent hydrocarbon, and there are no tests sufficiently delicate to detect traces of it in the presence of relatively large amounts of aldehyde. Quite recently, however, Newitt and Gardner [43*a*, 1936] have succeeded in isolating methyl alcohol in considerable quantities during the combustion of methane at ordinary pressure by so arranging the experimental conditions that the reaction can be arrested at an early stage.

The occurrence of carbon dioxide in the products under circumstances which preclude its formation by the direct oxidation of carbon monoxide and the absence of free hydrogen and carbon are all satisfactorily explained by the theory. Its application to the results of explosive combustion will be dealt with later.

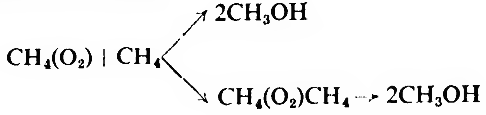
The Peroxide Theory. Mention has been made of the occurrence of peroxides during combustion and of the suggestion that the initial product of combustion of a hydrocarbon is an alkyl peroxide or alkyl hydrogen peroxide [36, 1930–3].

According to this view the oxidation of methane, for example, would proceed as follows:

1st stage: $CH_4+O_2 \rightarrow CH_4(O_2)$ or $CH_3{\cdot}O{\cdot}O{\cdot}H$

2nd stage: $CH_4(O_2) \rightarrow HCHO+H_2O$

The formation of methyl alcohol could result from the autoxidation of a methane molecule by its peroxide or by intramolecular change:



$$CH_4(O_2)+CH_4 \begin{cases} \nearrow 2CH_3OH \\ \searrow CH_4(O_2)CH_4 \rightarrow 2CH_3OH \end{cases}$$

Alkyl peroxides are usually unstable endothermic liquids which readily explode, giving a mixture of products including alcohols, aldehydes, and fatty acids; and since their decomposition may give rise to oxygen atoms or active molecules, there is no difficulty in postulating a chain mechanism based upon their initial formation and subsequent decomposition.

Egerton has made use of such a mechanism to explain the phenomenon of 'knock' in the internal combustion engine [20, 1928]. According to his view at that date:

> 'Suppose some fuel molecules are amongst oxygen and nitrogen molecules in a vessel the temperature of which is gradually rising. The molecules primarily pick up their energy from the walls. It is the walls that control affairs at first, and reaction only occurs at the walls at first. Sufficient of the fuel molecules in the body of the gas may, however, gain momentarily sufficient energy to unite with an energetic oxygen molecule with which they happen to encounter. Prof. Callendar and his associates have investigated this temperature of initial combustion. It means essentially that a temporary peroxide is formed —a peroxide in a high energy state possessing the energy of activation of the fuel and oxygen and also potentially the reaction energy.
>
> 'Several things may happen to this active addition compound of fuel and oxygen. (*a*) It may revert to a normal state and radiate energy in so doing, and form a stable peroxide. Peroxides are indeed found amongst products of combustion and of oxidation of organic compounds (as Wartenburg, Staudinger, Callendar and Mardles, and others have shown). (*b*) The compound may break up again, the parts being less active by the energy radiated. (*c*) The compound may reorganize and give highly active products, thus for ethane
>
> $CH_3{-}CH_3+O_2 \rightarrow CH_3{\cdot}CH_3{\cdot}O_2 \rightarrow CH_3{\cdot}CHO+H_2O.$
>
> (Dihydroxyethane may possibly also be formed to some extent as an intermediate stage in the production of the aldehyde and water.) (*d*) Collision may occur. Encounter with inactive nitrogen molecules may result merely in frittering down the energy of the active product, but encounter with a fairly active fuel molecule, or product thereof, or oxygen molecule, will raise its energy so that it will react and produce active products. These products in turn may collide and activate other fuel

molecules, and so on, a reaction chain mechanism being set up; in the above case of ethane,

$$CH_3-CH_3+O_2 \rightarrow CH_3CHO+H_2O,$$

the active aldehyde and/or water molecules being able to communicate their energy to activate other ethane molecules, and so on.

'Once a chain mechanism is established, local free energy increases, and molecules can be excited into higher energy states, and in returning from these states can give out light. So it is that luminescence can be observed during combustion of hydrocarbons many degrees below their igniting temperature.'

Although there is an apparent difference between the two theories outlined above, a closer examination will show little real distinction. For whereas the peroxide theory involves the formation of an alkyl peroxide by direct collision between a hydrocarbon and an oxygen molecule, the hydroxylation theory does not exclude a transient physical association between a hydrocarbon and an oxygen molecule until hit by a second hydrocarbon molecule, with consequent immediate formation of two molecules of the monohydroxy compound as the first recognizable chemical result.

The Atomic Chain Theory. Recently R. Norrish has proposed an 'Atomic Chain Theory' which, whilst differing from the hydroxylation theory in its explanation of the initial phase of oxidation, is in agreement with it in regard to the subsequent course of the combustion [46, 1935]. According to Norrish the oxidation of a hydrocarbon may be visualized in terms of a simple chain involving a hydrocarbon radical and an oxygen atom. Thus in the case of methane the chain mechanism would be:

$$CH_4+O = CH_2+H_2O+48 \text{ kg.-cal.} \qquad (1)$$

$$CH_2+O_2 = HCHO+O+15 \text{ kg.-cal.} \qquad (2)$$

This chain can continue until it is terminated by one or other of the following processes:

$$O+CH_4+X = CH_3OH+X^1+88 \text{ kg.-cal.} \qquad (3)$$

$$O+\text{surface} = \tfrac{1}{2}O_2.$$

The oxygen atoms necessary to initiate the chain are assumed to be formed by the productions of formaldehyde through a surface reaction

$$CH_4+O_2 \xrightarrow{\text{surface}} HCHO+H_2O$$

and the subsequent oxidation of formaldehyde to formic acid with liberation of an oxygen atom

$$H\cdot CHO+O_2 \rightarrow (H_2CO_3) \rightarrow H\cdot COOH+O.$$

Much of the atomic oxygen so formed will remain adsorbed and ultimately recombine on the surface—the remainder passing out into the gas phase and generating reaction chains. The induction period may therefore be identified with the time during which an equilibrium quantity of formaldehyde is being built up at the surface, and formaldehyde may be regarded as the initial product of the oxidation of methane.

The formation of methyl alcohol (and in the case of other hydrocarbons the corresponding alcohol) may be expected to occur to some extent by the operation of (3) under all conditions of slow combustion, but would be most marked at high pressures and in the presence of high concentrations of an inert gas. It can also be shown on the basis of the theory that the most reactive mixture should be one containing hydrocarbon and oxygen in the ratio 2:1.

For olefines the corresponding mechanism would be:

(1) During the induction period (taking ethylene as an example):

$$C_2H_4+O_2 = 2H\cdot CHO+118 \text{ kg.-cal.}$$

$$H\cdot CHO+O_2 = H\cdot COOH+O.$$

(2) During the reaction period:

$$C_2H_4+O = H\cdot CHO+CH_2+35 \text{ kg.-cal.}$$

$$CH_2+O_2 = HCHO+O+83 \text{ kg.-cal.}$$

The chain reaction can then continue until stopped by one of the following processes:

$$O+C_2H_4+X = C_2H_4O+X^1$$

or

$$O+\text{surface} = \tfrac{1}{2}O_2.$$

The atomic chain theory differs from the peroxide theory in that it postulates the propagation of reactivity by atoms and radicals and not by an *energy-chain mechanism* such as that originally proposed by Egerton in 1927. One of the consequences of this difference appears in the explanation given of certain aspects of the kinetics of combustion. Thus Norrish points out that the addition of an inert diluent gas to a medium reacting by an energy-chain mechanism should cause a slowing down in velocity, whereas in actual fact the reverse is usually the case. Pease and Munro have also found that, although peroxides are formed during the oxidation of propane, they are not essential to the chain propagating reaction, and when the experimental conditions are such as to preclude their formation only a moderate reduction in reaction velocity is observed. (For more recent views of Egerton and others on propagation of combustion by radical-chain rather than energy-chain mechanism see Article 1 in section on Detonation.)

Comparing the hydroxylation and atomic chain theories the main difference lies in the mode of formation of aldehyde; in the former aldehyde results from the further hydroxylation of an alcohol, whilst in the latter it results directly from the operation of the chain mechanism. The two schemes are mutually consistent if it be supposed that collision between an oxygen atom and a hydrocarbon molecule (C_nH_{2n+2}) produces a complex ($C_nH_{2n+2}O$) which may split to $[C_nH_{2n}]+H_2O$, the radical giving rise to reaction chains or becoming stabilized to the alcohol $C_nH_{2n+1}OH$ by a ternary collision. Thus in the case of methane

$$\begin{array}{c} CH_4+O_2 \rightarrow (CH_4O) \rightarrow \left\{\begin{array}{l} CH_2 \xrightarrow{+O_2} H_2CO+O \\ H_2O \end{array}\right. \\ \downarrow \\ CH_3OH. \end{array}$$

In this connexion it may be pointed out that Bone and Davis [8] concluded that the primary decomposition products of methyl alcohol at low temperatures are the radical CH_2 and steam, and it may well be that in the early stages of combustion the conditions are such that all three are present in the system in equilibrium proportion.

To summarize, it may be said that the hydroxylation theory accounts satisfactorily for all the analytical data of both slow and explosive hydrocarbon combustion although the mechanism by which the initial oxygen attack takes place is not specified.

The peroxide and the atomic chain theories, on the other hand, are concerned principally with the kinetic aspects of combustion and with the mechanism of the chain propagating reactions. The experimental evidence for this part of the subject, however, is still incomplete and in many cases unconvincing, and until more has been done it is impossible to predict to what extent either will afford a satisfactory explanation of all the essential phenomena.

B. EXPLOSIVE COMBUSTION

Before dealing with factors relating to the ignition and development of pressure in explosions of hydrocarbon-air (oxygen) media it remains briefly to show how the hydroxylation theory, having accounted for the course of the intermediate stages in the slow non-explosive combustion of hydrocarbons, was successfully applied by Bone and his collaborators [6, 1932] to account for the chemical processes occurring in flames and explosions. For, although the conditions prevailing in such circumstances are far more complex than those of slow combustion, the main course of the chemical changes concerned therein may be satisfactorily interpreted on the supposition that the result of the initial encounters between hydrocarbon and oxygen is the same in both, namely, the formation of an 'oxygenated' and usually a 'hydroxylated' molecule. At the higher temperatures of flames, however, secondary thermal decompositions come into play at an earlier stage, and play a more conspicuous part than in slow combustion; but there are the strongest reasons for the belief that they do not precede the reaction between hydrocarbon and oxygen molecules, but arise in consequence thereof.

In view of the complexities of flames and of the great difficulties in following by chemical analysis the course of events therein, the most that can be reasonably required of any acceptable theory is that in a general way it shall enable the main happenings in any particular case to be predicted; for it cannot be expected that in all circumstances the combustible molecules will combine with oxygen in precisely the same way and abnormalities may arise. It will suffice, therefore, to show how the normal occurrences are consistent with the theory as already outlined.

Thermal Decomposition of Alcohols and Aldehydes. It is necessary first of all to consider how the various oxygenated molecules intermedially formed might be decomposed in flames and, although in places our knowledge of such pyrolyses is incomplete, generally speaking the available information is adequate for the purpose. In particular it should be borne in mind (*a*) that the mode of decomposition of such compounds may vary with temperature and that the mean temperatures of flames show wide differences according as the composition of the explosive mixture concerned is near one or other of the limits of inflammability and also (*b*) that the extent of such decompositions is dependent upon pressure, a fact which may profoundly influence the course and temperature of combustion (see articles 'Combustion Phenomena at High Pressures' (p. 2884) and 'Ignition in Gases with Special Reference to Knock Problems' (p. 2958), Article 5, Detonation section.

Alcohols. At fairly low temperatures the vapours of primary alcohols decompose into steam and an unsaturated hydrocarbon molecule or residue, but at higher temperatures into hydrogen and the corresponding aldehydes. In intermediate ranges both changes may occur simultaneously, and in flames they are always followed by secondary decompositions and/or hydroxylations according to circumstances. Thus, for example, one might have:

$CH_3 \cdot OH$ primarily resolved into (i) $H_2C{:} + H_2O$ and/or (ii) $H_2C{:}O + H_2$ ($-9{\cdot}3$ cal.) followed by secondary resolutions of the $H_2C{:}O$ into $H_2 + CO$ (vide formaldehyde) and in favourable circumstances by hydrogenations of $H_2C{:}$ residues to CH_4.

C_2H_5OH primarily resolved into (i) $C_2H_4 + H_2O$ ($+7$ cal.) and/or (ii) $H_2 + CH_3 \cdot CHO$ (-10 cal.) followed by secondary resolutions of C_2H_4 into $C_2H_2 + H_2$ and/or $2C + 2H_2$, and of CH_3CHO into $CH_4 + CO$ and/or $C + 2H_2 + CO$ (vide acetaldehyde).

Aldehydes. At temperatures between about 400 and 600° C. aldehyde vapours containing one CHO group and one or more other carbon atoms are primarily resolved into CO and a saturated hydrocarbon; thus with *acetaldehyde*:

$$\text{(i)}\ CH_3 \cdot CHO = CH_4 + CO + 2\ \text{cal.}$$

With further rising temperature the breakdown becomes progressively more complex, tending at very high temperatures to some such final stage as

$$\text{(ii)}\ CH_3 \cdot CHO = C + 2H_2 + CO \ldots -19{\cdot}8\ \text{cal.}$$

It is important to note (i) that of all the oxygenated molecules known to be formed in slow combustion, the vapour of formaldehyde is pre-eminently that which at all temperatures in flames decomposes primarily into carbon monoxide and hydrogen (perhaps with a trace of methane) without any separation of carbon whatever, thus:

$$H_2C{:}O = H_2 + CO \ldots -13{\cdot}5\ \text{cal.}$$

Glyoxal vapour would probably be resolved at all temperatures into $CO + H_2C{:}O$ and secondarily into $2CO + H_2$, also without carbon deposition; but precise knowledge is lacking. Whenever the explosion of a hydrocarbon-oxygen mixture results in substantially nothing but carbon monoxide and hydrogen without carbon deposition, an intermediate formation of formaldehyde or glyoxal or both may be inferred.

Before dealing with the compositions of the explosion products as determined by Bone and collaborators [6, 1932; 11, 1927] it should be stated that the experiments have been concerned with gaseous hydrocarbons whose molecules contain not more than 4 carbon atoms; for beyond the C_2-members conditions get so complex and incalculable that the difficulties of chemical interpretation become insuperable, owing to the rapidly increasing number of possible secondary reactions masking the primary changes. Also, from a chemical point of view, most has been learnt from explosions of media containing no more oxygen than the $C_nH_m + \frac{n}{2}O_2$ proportion; when this is exceeded, all that can be revealed by chemical analysis is the operation of the water-gas reaction $CO + OH_2 \rightleftharpoons CO_2 + H_2$ during the cooling period.

Apart also from deductions drawn from the gaseous products of flames and explosions as to their origin in intermediate oxygenated bodies, there is no difficulty in demonstrating the actual existence of aldehydes in ordinary hydrocarbon flames. Bone and Drugman found them in the interconal gases when ethylene was burnt in air in a modified form of Smithells' separator as also in the condensed water formed when a steady flame of air (or oxygen) was maintained in an atmosphere of hydrocarbon or coal gas [11, 1927]. Their presence has also been proved in the explosion products of hydrocarbons such as ethane and ethylene with suitable defect of oxygen.

Explosions of Methane, Ethane, Ethylene, and Acetylene, each with its own Volume of Oxygen.

Methane. When a $CH_4 + O_2$ mixture is exploded in a glass bulb at atmospheric pressure, there is a sharp bluish flame without separation of carbon and some steam condenses on cooling. This result was first observed by John

Dalton [15, 1808], who found (*a*) the mixture to explode 'without any material change in volume', and (*b*) after removal of small amounts of carbonic anhydride the residue 'to possess all the characteristics of equal volumes of carbonic oxide and hydrogen'. This result is what might have been predicted from the 'hydroxylation' theory supposing a 'non-stop' run through the mono- to the dihydroxy stage followed by a complete breakdown of formaldehyde into carbon monoxide and hydrogen and a subsequent 'water-gas reaction' during the cooling, thus:

$$CH_4 \rightarrow CH_3OH \rightarrow \underbrace{CH_2(OH)_2}_{H_2O+\underbrace{H_2:C:O}_{H_2+CO}}$$

and $$CO+OH_2 \rightleftharpoons CO_2+H_2.$$

Although at atmospheric pressure methane-oxygen mixtures containing less than 40% of oxygen are non-explosive. by sufficiently raising the pressure they become so down to about the 70 CH_4/30 O_2 proportion; reference to the explosion of such media will be found.elsewhere (p. 2892).

Ethane. The explosion of an equimolecular mixture of ethane and oxygen was pointed out by Bone to be crucial as between the former idea of a preferential burning of the carbon and the 'hydroxylation' theory. For whereas, according to the former, only carbon monoxide and hydrogen should result, thus:

$$C_2H_6+O_2 = 2CO+3H_2, \quad \text{with} \quad p_2/p_1 \quad 2{\cdot}5,$$

the 'hydroxylation' theory would require the formation of methane, carbon, hydrogen, carbon monoxide, and steam with some carbon deposition and a p_2/p_1 ratio materially less than 2·5, as follows:

$$C_2H_6 \rightarrow C_2H_5OH \rightarrow \underbrace{CH_3\cdot CH(OH)_2}_{\underbrace{H_2O+CH_3\cdot CHO}_{\underbrace{CH_4+CO}_{C+2H_2,\ \&c.}}}$$

Actually, when exploded in a glass bulb a lurid yellowish-red flame fills the vessel, accompanied by a black cloud of carbon and considerable condensation of water, which, if tested with Schiff's reagent, is found to contain aldehydes. The cold gaseous products show a p_2/p_1 ratio = 1·5, and their composition on analysis is found to be as follows:

$$CO_2 = 4{\cdot}2,\ CO = 33{\cdot}5,\ C_nH_m = 2{\cdot}7,\ CH_4 \quad 11{\cdot}0,\ \text{and}\ H_2 = 48{\cdot}6;$$

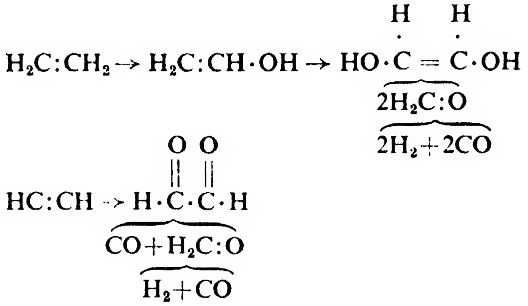
also about one-sixth of the original carbon is deposited, all of which is in conformity with the hydroxylation theory. When fired in vessels of different surface/volume ratios, or even when detonated in a lead coil, similar results are obtained with variations readily attributable to the peculiarities of temperature, rate of cooling, &c., pertaining to each particular case.

Ethylene and Acetylene. When equimolecular mixtures with oxygen of these hydrocarbons are exploded in glass bulbs at initial pressures of 500 and 300 mm. respectively, in neither case is there any carbon deposition or condensation of steam on cooling, which is in striking contrast with the behaviour of the $C_2H_6+O_2$ mixture. The pressure of the gaseous products is almost doubled with (*a*) the $C_2H_4+O_2$ mixture and increased by nearly 50% with (*b*) the $C_2H_2+O_2$ mixture, the compositions being as follows:

(*a*) $CO_2 = 0{\cdot}5$, $CO = 50{\cdot}0$, $H_2 = 47{\cdot}5$, and $CH_4 = 2{\cdot}0\%$ with $p_2/p_1 = 1{\cdot}95$.

(*b*) $CO_2 = 0{\cdot}75$, $CO = 67{\cdot}0$, $H_2 = 30{\cdot}75$, and $CH_4 = 1{\cdot}5\%$ with $p_2/p_1 = 1{\cdot}47$.

While the behaviours of these two hydrocarbons would lend apparent support to a preferential burning of carbon, the experimental results are just what would be predicted from the hydroxylation theory as follows:



$$H_2C:CH_2 \rightarrow H_2C:CH\cdot OH \rightarrow \underbrace{HO\cdot\overset{H}{\dot{C}} = \overset{H}{\dot{C}}\cdot OH}_{\underbrace{2H_2C:O}_{2H_2+2CO}}$$

$$HC:CH \rightarrow \underbrace{H\cdot\overset{O}{\overset{\|}{C}}\cdot\overset{O}{\overset{\|}{C}}\cdot H}_{CO+\underbrace{H_2C:O}_{H_2+CO}}$$

Perhaps the most significant feature of the experimental evidence is that, whereas all the gaseous hydrocarbons of the C_nH_{2n} series (i.e. ethylene, propylene, trimethylene, and butylene) on explosion with a proportion of oxygen $C_nH_{2n}+n/2\,O_2$ always yield substantially carbon monoxide and hydrogen only, without any separation of carbon or material steam formation as though there had been a preferential burning of their carbon in accordance with the equation

$$C_nH_{2n}+n/2\,O_2 = n(CO+H_2),$$

explosions of the corresponding members of the C_nH_{2n+2} or paraffin series (e.g. ethane, propane, butane, &c.), with oxygen in the $C_nH_{2n+2}+n/2\,O_2$ proportion, all result in dense clouds of carbon steam, methane, and oxides of carbon, just as with the $C_2H_6+O_2$ mixture.

These results are consistent with the theory which would require separation of carbon, and much steam, as well as some aldehyde survival in the paraffin explosions, while the corresponding olefine explosions are explained on the supposition of their substantially involving successive eliminations of $H\cdot\underset{\bullet}{\dot{C}}\cdot OH \rightarrow H_2CO$ (formaldehyde) groups which, rapidly decomposing in the flame, yield (as does formaldehyde) equal volumes of carbon monoxide and hydrogen without carbon separation or steam formation.

In addition to these experiments which have been specifically referred to, many others embracing all conditions between slow combustion and detonation and at initial pressures ranging between one-third of an atmosphere up to 50 atm. have all been in accordance with the hydroxylation theory.

Ignition Phenomena.

In order to initiate flame in a mixture of a hydrocarbon and air (oxygen) it is necessary that (*a*) its composition should lie within a range of mixtures bounded by lower and upper 'limits of inflammability' applicable to the experimental conditions, and (*b*) a sufficient volume of it should either be raised by the application of some external source of heat at least to its ignition temperature or that it should be sufficiently energized by an electric spark. The phenomena associated with the spontaneous ignition of hydrocarbon-air media (but principally at high pressures) have been discussed in some detail in another contribution

(p. 2958), and reference has been made to the low-pressure ignition phenomena observed by Neumann and Egorow [41, 1932] (pp. 2863–4). Up to the present no comprehensive investigation has been undertaken covering all the features of spontaneous ignition of selected explosive mixtures over a pressure range extending from very low pressures of a few millimetres of mercury up to high pressures of several atmospheres, and a complete understanding of the subject is therefore difficult. Moreover, so far as we are aware, in no instances have the media selected for investigation at very low pressures corresponded with those studied elsewhere at high pressures. In order to clarify the position we have prepared a hypothetical diagram (Fig. 10) intended to indicate comprehensively the probable behaviour of higher paraffin hydrocarbon-air (oxygen) mixtures, &c., over such a pressure range.

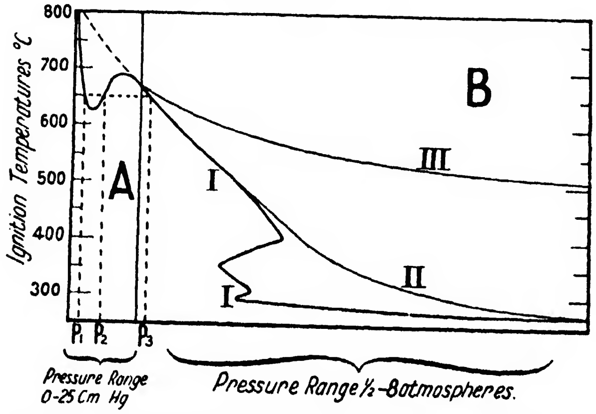


FIG. 10. The relationship between spontaneous ignition temperatures at reduced (*A*) and high (*B*) pressures.

The left-hand side of the diagram, *A*, which has been drawn to a larger pressure scale than that employed on the right, *B*, is representative of the behaviour found at very reduced pressures. Thus the typical explosive mixture will ignite spontaneously if admitted to an evacuated vessel maintained at, say, 650° C. if its pressure is not less than p_1 mm. of mercury. This pressure is frequently referred to as the 'lower explosion limit'. If the pressure of admission be further increased, ignition will occur with a decreasing time lag (see p. 2863), but at pressures above p_2 mm. of mercury it will no longer do so. This pressure is known as the 'upper explosion limit'. At some still higher pressure p_3, located in the high-pressure area, *B*, a third limit is found at pressures above which ignition will always occur. It may here be pointed out that the term 'low-pressure explosion limits' should not be confused with 'limits of inflammability' with which we shall shortly deal; a better designation would be 'low-pressure *ignition* limits'.

Low-pressure ignition limits have not so far been studied extensively with hydrocarbon media and observations have been limited to methane and ethane (Neumann and Egorow [41, 1932]; Kowalsky, Tschirkow, and Sadownikow [31, 1932]; Neumann and Andrejew [40, 1933]); but the phenomenon seems well established with hydrogen, carbon monoxide, carbon disulphide, phosphine, &c., and there seems no reason to suppose it to be other than general. Usually the limits are not observable with mixtures outside certain ranges of composition; the ignition-point curve is then smooth, as depicted by the dotted line in the region *A*.

The existence of low-pressure ignition limits has contributed materially to the development of the theory of chain reactions (p. 2861). Thus at pressures below p_1 it is thought that chains are broken by frequent collision with the walls of the containing vessel at a rate greater than they can be propagated in the gas phase. At p_1 the chains surviving in the gas phase just exceed those broken on the walls, so that a slow reaction is changed very abruptly into a very rapid one. This view is supported by the fact that addition of an inert gas which would prevent diffusion of chains to the walls lowers the limit, whereas a reduction in the diameter of the containing vessel which would facilitate chain-breaking raises the limit.

The precise mechanism of the upper ignition limit (p_2) is not yet entirely agreed upon, but it is generally accepted as being due to the incidence of a gas-phase deactivation and probably to triple collisions. This is supported by the fact that in this case an addition of inert gas to the medium narrows the limit.

Passing to the higher pressure region, *B*, it is thought that with increasing pressure conditions no longer remain essentially isothermal, so that with a general preflame rise in temperature fresh chains are initiated in the explosive medium, and at p_3 ignition can again be effected.

The influence of still further increase in pressure on the ignition points seems to depend on the character of the hydrocarbons concerned. Curve 1 is representative of the higher paraffins. The naphthenes yield similar ignition-point curves, but the fall to the 300–400° C. range is not as abrupt as is found with the paraffins. The simpler olefines, e.g. ethylene, exhibit a smooth curve of the type depicted by curve 2, and the ignition points of aromatic hydrocarbons are usually higher (curve 3). Generally it seems probable that the characteristics of spontaneous ignition under pressure depend upon the nature and speeds of formation and further oxidation of products intermedially formed in each particular case, a matter to which we have already referred elsewhere in regard to the paraffins (p. 2968).

Limits of Inflammability. An inflammable or explosive mixture may be defined as one through which flame can be propagated independently of, and away from, the original source of ignition. With mixtures of any particular combustible gas or vapour and air (oxygen) there are, under given physical conditions, certain limits of composition within, but not outside of which, self-propagation of flame will take place after ignition has been effected. These limits defined in terms of the percentage of the combustible gas present are usually referred to as the 'lower' and 'upper' limits of inflammability, respectively, of the gas under given conditions. For any particular gas, however, they vary with the position of the source of ignition, since the progress of flame may be assisted or retarded by convection currents, according as it has to pass in an upward, horizontal, or downward direction. Thus, for example, for methane-air mixtures, at atmospheric pressure and temperature, the limits for different directions of propagation are as follows:

	Direction of Propagation		
	Upward	*Horizontal*	*Downward*
Lower limit . .	5·35	5·40	5·95
Upper limit . .	14·85	13·95	13·35

In the following table are given the limits of the principal hydrocarbons in air determined by A. G. White [58, 1924] for upward propagation in a glass tube 7·5 cm. in diameter.

	Lower	*Upper*
Methane	5·35	14·85
Ethane	3·12	14·95
Pentane	1·42	8·0
Benzene	1·41	7·45
Toluene	1·27	6·75
Ethylene	3·02	34·0
Propylene	2·18	9·7
Butylene	1·70	9·0
Acetylene	2·60	80·5

R. V. Wheeler and collaborators [57, 1918] gave the following figures, the criterion of inflammability being propagation of flame through a 2½-litre sphere with central ignition.

	Lower	*Upper*
Methane	5·6	14·8
Ethane	3·1	10·7
Propane	2·2	7·4
Butane	1·7	5·7
Pentane	1·4	4·5
Ethylene	3·0	22·0
Acetylene	3·3	52·3
Benzene	1·5	5·6
Toluene	1·4	5·4

It may be noted in passing that in a homologous series the range of inflammability narrows progressively as the combustible increases in molecular weight; thus the range 5·4–14·8% for methane may be contrasted with approximately 1·2–4·2 for hexane.

Also when endothermic combustibles, e.g. acetylene, are considered, the range is very much wider owing to their exothermic decomposition in combustion.

In circumstances where it is possible to propagate cool flames of incomplete combustion (vide p. 2868) the upper limit may be considerably widened, and with mixtures of ethyl ether and air there are at atmospheric pressure two ranges of inflammability for horizontal propagation (1·88–9·45 and 19·0–34·0%) separated by a range which will not propagate flame, the higher of the two ranges relating to 'cool flames'.

If oxygen be employed as the supporter of combustion instead of air the upper limit is also raised appreciably; this may be illustrated by the following figures due to Terres [11, 1927]:

	Air		*Oxygen*	
	Lower	*Upper*	*Lower*	*Upper*
Methane	6·3	11·9	6·5	51·9
Ethane	4·2	9·5	4·1	45·8
Ethylene	4·0	14·0	4·1	61·8
Acetylene	3·5	52·3	3·5	89·4

These figures were determined in a burette, 19 mm. in diameter, and relate to downward propagation.

A. G. White [59, 1924] has also shown the influence of temperature upon the ranges of various gas-air mixtures which will propagate flame downwards in a tube 25 mm. in diameter.

Temp. ° C.	*Methane*		*Ethylene*		*Acetylene*	
	Lower	*Upper*	*Lower*	*Upper*	*Lower*	*Upper*
17	6·3	12·9	3·45	13·7	2·90	55·0
100	5·95	13·7	3·20	14·1	2·68	65·0
200	5·50	14·6	2·95	14·9	2·39	81·0
300	5·10	15·5	2·75	17·9	2·19	..
400	4·80	16·6	2·50	..	..	..

Increase of pressure may also appreciably affect ranges of inflammability, a matter to which we have referred elsewhere ('Combustion Phenomena under Pressure', p. 2887).

Pressure Development in Explosions of Hydrocarbon-Air Media.

Under ideal conditions the rate of pressure development and the magnitude of the maximum pressure in a gaseous explosion would always be characteristic of a given mixture, dependent only on its mode of combustion and the initial pressure at which it is fired. Unfortunately it is never possible to realize completely such ideal conditions because the development of an explosion is influenced by the size and shape of the explosion vessel employed, factors which also affect the conduction and radiation losses. When a gaseous explosive medium is ignited there may happen (i) a short 'induction period', then (ii) a pressure rise up to a certain maximum ('explosion period'), and finally (iii) a 'cooling period'. Whether or not in any particular case the attainment of maximum pressure synchronizes precisely with the moment when the flame reaches the walls and completely fills the chamber depends so much on circumstances that no general rule can be laid down; but it seems reasonable to suppose that the faster the explosion the more nearly will such synchronization be attained, assuming that the chamber be not too large. Much depends on the shape of the explosion chamber.

The general effect of any cooling by conduction during the 'explosion period' is a lowering of the maximum pressure (temp.) attained and a tendency to temperature gradients in the medium at the moment of maximum pressure and subsequently during the 'cooling period'. Such cooling influence of the walls in any particular case probably varies directly with the surface/volume ratio of the bomb and inversely with the initial firing pressure; it is also materially influenced by the degree of agitation of the medium. The principal factor, however, is the duration of the 'explosion period'.

During the whole of the 'explosion period' and well into the subsequent 'cooling period' the gaseous medium is also losing energy by direct 'radiation' to the chamber walls where absorption occurs unless the surface be polished so as to be highly reflecting. Indeed a certain fraction of the total energy developed on explosion is always lost to the system by radiation and never appears at all as kinetic (temperature or pressure) energy in the medium. It is estimated that of the total radiation emitted in flames and explosions, upwards of 95% is in the infra-red, and this has been shown by Julius [30, 1890] to be attributable to incipiently formed (or forming) carbon dioxide and steam molecules. Such emission occurs in well-defined bands: in the case of carbon dioxide mostly at 4·4μ, and to a less degree at 2·7μ, and with steam mostly at 2·8μ.

R. von Helmholtz has given the following figures for the relative amounts of radiation per litre of gas burnt, emitted by flames of given size, the air-supply in each case being adjusted so that the flame was just non-luminous:

	Relative radiation per litre
Hydrogen	74
Carbon monoxide	177
Methane	327
Ethylene	570

From such figures it would appear that the radiating power of a hydrocarbon is due to the number of carbon dioxide and steam molecules produced. Thus with methane: $177+(2\times 74) = 325$. This aspect of the subject has been examined recently by Haslam, Lovell, and Hunneman [26, 1925], however, who measured the radiation from flames of theoretical mixtures with the aid of methane and carbon monoxide, and found that the intensity of radiation from steam was 1·7 times that from carbon dioxide; the subject therefore needs further exploration.

Helmholtz took the view that the radiation from such flames is due to chemical rather than to thermal cause. Paschen and others have maintained that it is purely thermal. It seems now generally recognized that, as the outcome of the initial encounters between the molecules concerned, the radiation emitted is probably of chemical origin (chemi-luminescence). After a state of molecular equilibrium has been attained, however, it is probably controlled by temperature alone. In luminous flames, in addition to chemical radiation, there is also that emitted by incandescent carbon. This black body radiation obeys the Stefan-Boltzmann law and is therefore proportional to T^4.

Very little experimental work has been undertaken in connexion with conduction and radiation losses from flames and explosions of single hydrocarbon-air (oxygen) media, but their general quantitative influences may perhaps be judged from the following figures due to David [16, 1920–5] and Bone and Townend [11, 1927] for a 12·4% coal gas-air mixture exploded in a cylindrical explosion vessel 12×12 in.:

Relative Heat Losses by Conduction and Radiation in the Explosion of a 12·4% Coal Gas-Air Mixture at Atmospheric Pressure (David)

Time after ignition, sec.	*Mean gas temperature, ° Abs.*	*Heat loss expressed as a percentage of heat of combustion of coal gas*		
		Conduction	*Radiation*	*Total*
0·08	2,050 (max. temp.)	5·5	4·5	10·0
0·1	2,030	6·8	5·8	12·6
0·2	1,800	17·4	13·0	30·4
0·3	1,610	25·0	17·2	42·2
0·5	1,330	34·0	21·4	55·0

At temperatures below about 900° C. the emission of radiation becomes negligible, and cooling is then effected solely by conduction. The total radiation loss throughout a coal gas-air explosion was found by David to be about 25%, varying slightly with mixture composition. The loss up to the moment of maximum pressure was proportional to the product of the third power of the maximum absolute temperature attained in the explosion and the time taken to attain the maximum pressure. With hydrogen-air mixtures the total radiation loss varied between 8 and 16%.

Callendar found an emission equivalent to 10–15% of the heat of combustion for coal gas-air flames as the diameter of the burner was increased from 1 to 4 in.; also the emission from a mass of radiating gas 100 cm. in depth at atmospheric pressure was within ½% of that from an infinite depth. If the pressure were increased to 20 atm., the like emission would be obtained from a depth of 5 cm. only. It is clear, therefore, that the radiation loss expressed as a percentage of the heat of combustion of the explosive mixture tends to become less important in very large explosion vessels or in explosions at high pressures.

Enough has been said to emphasize the importance in comparing both maximum explosion pressures and the times of attainment thereof of taking due consideration of the dimensions of the explosion vessel employed in each particular case and also of the relative position therein of the igniting source. Only where a study of the cooling losses has been made and the experimental values corrected accordingly can the values for any particular explosive mixture determined in one investigation be compared with those in another.

It should here be stated that a large amount of experimental data relating to explosions of hydrocarbon-air (oxygen) mixtures was determined by the French pioneers Berthelot and Vieille, and Mallard and Le Chatelier (1880–5) and, although much has never been repeated, it may now be regarded as mainly of historic interest (see, however, *Flame and Combustion in Gases*, chapter xix [11, 1927]).

In the course of an extensive series of explosion experiments carried out by R. W. Fenning [22, 1924–6] at the National Physical Laboratory, the hydrocarbons methane, benzene, and hexane, as well as a commercial petrol, were investigated. The explosion vessel employed was cylindrical in shape, being 7 in. in diameter and 8 in. long. It could be heated by means of a nichrome wire winding mounted on mica so that initial temperatures up to 400° C. could be employed. The indicator consisted essentially of a solid rimmed plane diaphragm 0·07 in. in thickness and 1½ in. in diameter, the deflexions of which were transmitted to a mirror lever of the Petavel type. Pressure-time records were made in the usual way on rapid sensitive paper, the moment of sparking being also recorded.

In Fig. 11 a series of pressure-time records is shown illustrating the effect of varying the mixture strength of methane-air mixtures between 7·3 and 12·1% of the combustible fired at 100° C. and at an initial pressure of 95 lb. per sq. in.

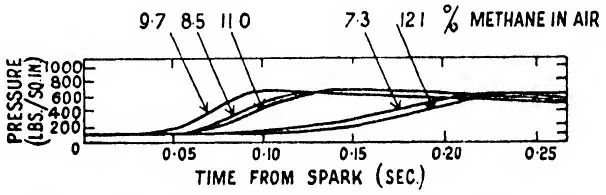


FIG. 11. Explosion records of methane-air mixtures (Fenning).

The numerical data as to 'explosion time' and 'pressure rise' are best illustrated by the two curves in Fig. 12. Mixtures containing from 9·7 to 10·5% of methane gave about the same pressure rise on explosion, whereas the 'explosion time' was a minimum in the region of the 9·7% mixture. The fastest burning mixture and that developing the highest pressure thus contains a small excess over the theoretical proportion of the combustible; this result is in accord with general experience.

The respective influences of varying initial pressure and

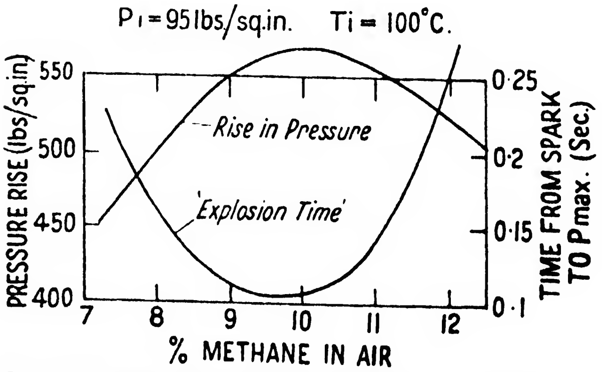


FIG. 12. Influence of mixture composition on explosions of methane-air mixtures (Fenning).

temperature were determined with a 9·9% methane-air mixture and the results summarized in the following table:

Initial temperature, ° C.	Initial pressure lb. per sq. in.	Maximum pressure lb. per sq. in.	$\frac{P_m}{P_i}$*	Time of attainment of maximum pressure, sec.	
				From spark	From start to rise
24·7	30·3	252	8·57	0·0997	0·0778
24·6	53·0	446	8·65	0·1163	0·0963
100	38·1	259	8·51	0·0798	0·0614
100	66·7	460	8·62	0·0933	0·0812
100	95·0	660	8·71	0·1090	0·0918
200	48·2	270	8·57	0·0682	0·0525
200	84·4	477	8·64	0·0750	0·0669
200	120·6	684	8·69	0·0838	0·0726
300	58·2	273	8·36	0·0496	0·0405
300	102·3	486	8·48	0·0597	0·0512
300	145·9	701	8·57	0·0671	0·0591
400	68·5	282	8·30	0·0410	0·0360
400	120·1	495	8·30	0·0473	0·0408
400	171·5	719	8·56	0·0548	0·0465

* These values, in order to be comparable among themselves, are corrected as follows:

$$\frac{P_m-(P_i-P_i\text{ corrected})}{P_i\text{ corrected}}$$

where P_i corrected = the initial pressure corrected to 15° C.

Raising the initial temperature at a given pressure was found to diminish the time required for the attainment of maximum pressure, a result which might be anticipated, seeing that in such explosions the rate of flame propagation probably depends largely upon 'conduction' of heat from layer to layer of the medium. As regards initial pressure, while Fenning's figures for this particular mixture show the 'explosion times' to increase with rise in initial pressure, no general conclusions should be drawn as to the influence of pressure as with other mixtures the reverse effect is found. We have dealt with this matter elsewhere (article, 'Combustion Phenomena under Pressure').

The investigations with benzene, hexane, and petrol were undertaken with a view to throwing some possible light on 'knock' in petrol-air engines. First of all a series of experiments was carried out at an initial temperature of 100° C. and a pressure of 95 lb. per sq. in. in order to study the effect of varying mixture strength in each case. It was found that with all three fuels rich mixtures gave rise to 'knock', the intensity of which varied as the air to fuel ratio, and the knock appeared to be preceded by high-frequency vibrations.

The relevant data have been summarized in the table in the next column.

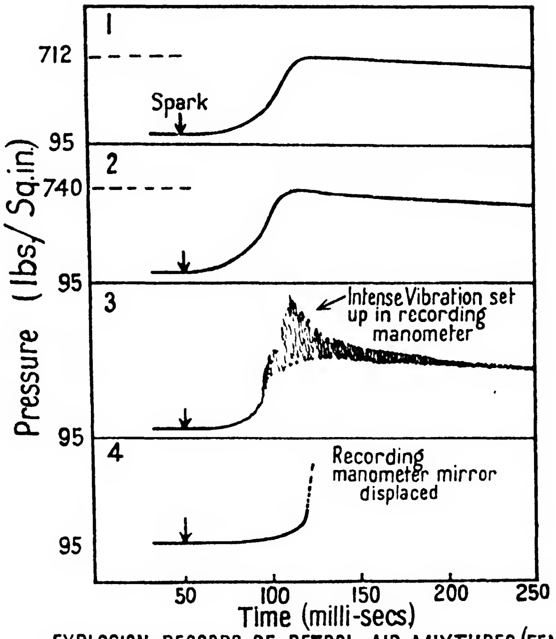
The pressure-time records shown in Fig. 13 illustrate the effects found with air-petrol mixtures whose air/fuel weight ratio varied from 14·8 to 8·9. The violence associated with the pressure rise when knock occurs is well brought out in the two lowest records.

It was also found that, whereas on raising the initial temperature to 300° C. the 'knock' occurring with rich mixtures was suppressed in the case of benzene, it persisted in hexane- and petrol-air mixtures.

With theoretical mixtures of all three fuels the explosion time diminished as the initial temperature was raised but increased with the initial pressure, the rate of increase with pressure decreasing at higher initial temperatures. Raising the initial temperature of the theoretical air-petrol and air-hexane mixtures led to knock of increasing intensity, the defect first appearing at the higher initial pressures and extending to lower ones as the initial temperature was raised. With the theoretical benzene mixture there was no indication of the incidence of knock with increase of initial temperature.

Explosions of Benzene-, Hexane-, and Petrol-Air Mixtures at Ti = 100° C. and Pi = 95 lb. per sq. in.

Mixture ratio air/fuel by weight	$\frac{P_{\text{max}}}{P_{\text{initial}}}$	Explosion time, millisec.
	Benzene	
16·84	8·28	105·1
14·76	9·00	73·5
13·24	9·50	59·7
13·16	9·50	59·8
12·06	9·74	55·1
10·7	9·78	49·0
9·15	Loud knock	..
	Hexane	
16·91	8·86	91·2
14·80	9·48	69·5
13·97	9·56	64·0
13·20	9·50	58·6
10·72	Loud knock	..
	Petrol	
19·2	7·74	175·2
16·9	8·58	109·6
14·8	9·33	78·4
13·0	9·71	67·1
10·7	Loud knock	..



EXPLOSION RECORDS OF PETROL-AIR MIXTURES (FENNING)
Ti = 100°C Pi = 95 lbs./sq. in.
AIR/FUEL WEIGHT RATIO: 1-14·8; 2=13·0; 3=10·7; 4=8·9.

FIG. 13.

It may also be observed from the previous table that the $P_{\text{max}}/P_{\text{initial}}$ values are much the same with all three fuels. Apart from their respective influences in regard to knock, changes of initial temperature and pressure also showed similar effects in each case and are best illustrated by the graphs (Fig. 14) for a 12 to 1 by weight air-benzene mixture. These show the effect on 'pressure rise' and 'explosion' times of increasing the initial pressure from 35 to 150 lb. per sq. in. at temperatures of 100°, 200°, and 300° C.

In 1927 G. B. Maxwell and R. V. Wheeler [38] published an account of explosion experiments on mixtures with air of the paraffins methane, ethane, propane, butane, and pentane, carried out in a 4-litre spherical bomb, ignition being effected at the centre of the vessel.

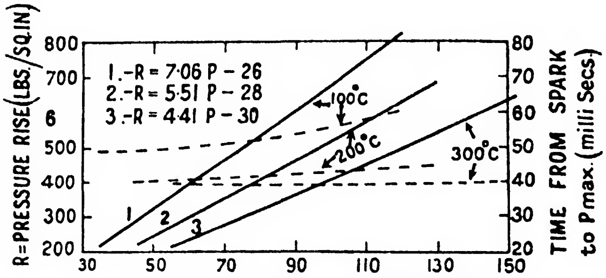


Fig. 14. Influence of initial pressure and temperature on explosions of a 12 to 1 (by weight) air-benzene mixture (Fenning).

In Fig. 15 curves have been plotted showing the 'pressure rises' (above atmospheric) and the explosion times for each of the five paraffins referred to. With each hydrocarbon, the mixture giving the maximum pressure contained a small excess of combustible over the theoretical proportion for complete combustion as follows:

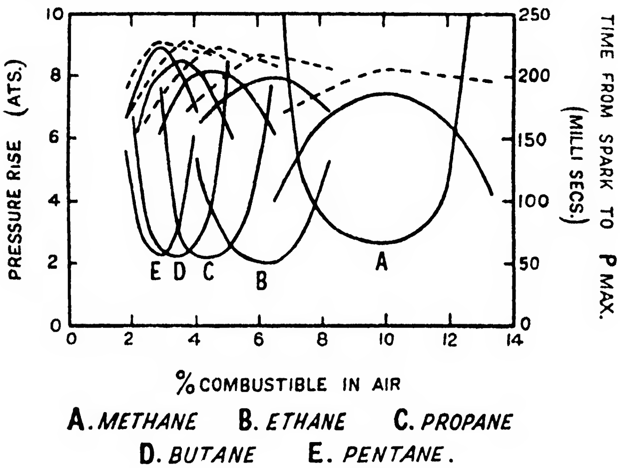


Fig. 15. Influence of mixture composition on explosions of paraffin-air mixtures (Maxwell and Wheeler).

	Theoretical mixture for complete combustion	*Mixture giving maximum pressure*
Methane	9·47	10·00
Ethane	5·64	6·30
Propane	4·02	4·60
Butane	3·12	3·65
Pentane	2·55	2·95

The theoretical maximum pressures and temperatures, i.e. if there has been no heat loss, were calculated in accordance with the method of H. T. Tizard and D. R. Pye [55, 1924] which (*a*) makes an allowance for the dissociation of steam and carbon dioxide at the maximum temperature attained using N. Bjerrum's values for the dissociation constants and thus introduces a correction for the precise number of molecules at $P_{\max}$, and (*b*) uses M. Pier and N. Bjerrum's values of the mean heat capacities of the explosion products from 15° C. to $T_{\max}$ (see *Flame and Combustion in Gases*, chapter xxi [11, 1927]).

These calculated values also predicted a maximum pressure for mixtures containing a small excess of combustible over the theoretical proportion, and the authors confirmed the view of Tizard and Pye that the effect is due to a suppression of dissociation by the presence of an excess of the combustible. Another factor should not be lost sight of, however, namely, that with explosive mixtures of a combustible with air, owing to the large dilution with nitrogen, the most reactive mixture from the point of view of 'active mass' contains an excess of combustible; if such a mixture burns faster on this account, cooling losses would be relatively less and the maximum pressure attained apparently greater.

The dotted curves (Fig. 15) show the so-calculated pressures, from which it may be noted that the difference between the observed and calculated values is greatest with methane- (9·8%) and least with pentane-air mixtures (2·45%). The authors discussed in their paper the various factors, e.g. conduction and radiation losses, incomplete combustion, errors in the values of dissociation constants and heat capacities, &c., which may contribute to the differences referred to; all these are matters, however, on which our understanding is still incomplete.

In a later paper Maxwell and Wheeler [38, 1929] described a parallel set of experiments with the olefines ethylene, propylene, and butylene, the data concerning which are shown graphically in Fig. 16. As with the paraffins, there was with each hydrocarbon a marked displacement of the maximum pressure mixture from the 'theoretical' mixture towards mixtures containing excess of hydrocarbon. The differences between the theoretical pressures calculated according to the method of Tizard and Pye and the experimental values were found to be greater than with the paraffins, being for the maximum pressure mixtures 13·6, 16·5, and 14·0% with ethylene, propylene, and butylene respectively; the explanation of this, however, again remained uncertain owing to the many factors involved.

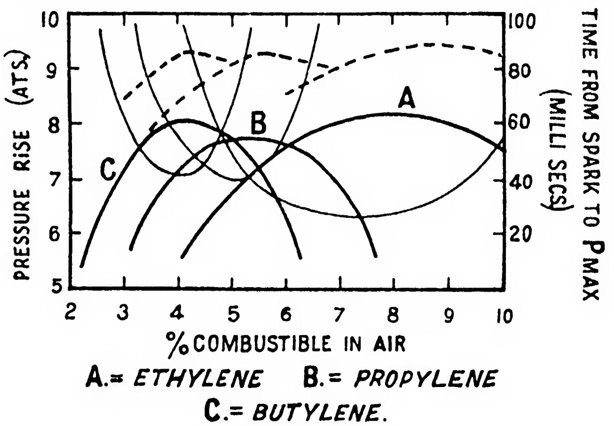


Fig. 16. Influence of mixture composition on explosions of olefine-air mixtures (Maxwell and Wheeler).

In other experiments [39, 1928] in a stainless steel explosion cylinder 6 in. diam. by 15 in. in length provided with a window fitted along one side the authors made photographic records of flame movement as well as time-pressure records of explosions of certain pentane- and benzene-air mixtures. It was found under such conditions that in a knocking explosion (cf. Fenning's pressure-time records), as was the case with a 3·3 pentane-air mixture at 2 atm., initial pressure combustion was not complete in the flame front nor was it continuous behind the flame. It appeared as though some impetus was required to complete the chemical reaction, and this occurred when a shock wave was produced when the accelerating and vibrating flame was arrested at the end of the cylinder (cf. article by R. P. Fraser, 'Flame Movement . . . &c.', Detonation section, p. 2983) the combustion being then completed almost instantaneously throughout the cylinder with consequent sudden development of pressure. In non-knocking explosions such as those of benzene-air mixtures or of pentane-air mixtures (*a*) at lower pressures, (*b*) with an anti-knock admixed, or (*c*) rendered turbulent by means of a fan, the combustion was continuous, and completed behind the flame front. How far such results are applicable to 'knock' in internal-combustion engines remains uncertain, but they show the importance of bearing in mind the fact that the progress of combustion in hydrocarbon flames is not always a continuous single-stage process (cf. Article 5, 'Ignition in Gases . . . &c.', in Detonation section, p. 2958).

A series of eight papers by S. Brown and collaborators published during the years 1925–9 [13] dealt with many factors influencing the nature of pressure development in explosions of higher hydrocarbon-air media and should be consulted by the reader interested in this branch of the subject. In particular it was found with hexane-air mixtures that, while raising the initial temperature generally effected a speeding up of the rate of pressure development, an optimum temperature existed for each mixture above which the reverse occurred.

As regards pressure development the following values were found for mixtures with air giving the highest pressure for each particular hydrocarbon. The explosion bomb employed had a cylindrical cavity 2·75 in. diam. and 7 in. long, ignition being effected at the centre and the mixtures fired at atmospheric pressure and temperature.

	Max. pressure lb. per sq. in.	*Explosion time, sec.*
n-Hexane . .	675	0·0195
n-Heptane . .	655	0·0175
n-Octane . .	668	0·0165
Benzene . .	665	0·0153
Toluene . .	650	0·0170
Xylene . .	675	0·0190

In the last paper of the series photographic records were reproduced showing the nature of flame movement in explosions occurring under engine conditions. From the point of view of 'knock' such factors were studied as an addition of an anti-knock to the medium and the auto-ignition of the unburnt mixture ahead of the flame by means of artificial 'hot spots', &c.; general deductions were also made in regard to the relation between 'knock' and both rate of rise pressure and the production of shock waves. Other investigations of this character which are beyond the immediate scope of our present article were those of L. Withrow and T. A. Boyd [60, 1931], C. F. Marvin and R. D. Best [37, 1931], and Duchene [18, 1931].

The Temperature of Hydrocarbon Flames.

The only *direct* methods available of measuring flame temperatures, namely, those using platinum resistance thermometry or thermojunctions, are unfortunately limited to temperatures below the melting-points of the platinum or platinum alloys employed. Moreover, such determinations are subject to various errors due to radiation and conduction losses for which it is difficult to allow. One way of applying such corrections, employed by Waggener (1896), consists in using a series of thermojunctions of wires of diminishing diameters; and, after plotting on a curve temperatures against diameters, to extrapolate so as to find the temperature at an infinitely small diameter. Another method, adopted by Berkebusch (1899), is to pass through the couple a known electric current which by previous trial in a vacuum has been found to be sufficient for the purpose. The investigators referred to limited their observations to the temperatures of bunsen coal-gas flames, the highest temperatures recorded being 1,770 and 1,830° C. in the two investigations respectively.

The principal *indirect* methods are (*a*) calculation of the temperatures from the pressures developed in gaseous explosions, and (*b*) the spectral line reversal method. The first of these has been used extensively, for provided the 'explosion time' is short so that cooling losses are small, and also that the composition of the gases at the maximum temperature can be estimated accurately (i.e. making due allowances for dissociation), $T_{\max}$ is calculable as follows:

$$T_{\max} = \frac{P_{\max}}{P_{\text{init.}}} \times T_{\text{init.}} \times \frac{m}{n},$$

where m/n represents the ratio of the number of molecules before and after explosion. In the hands of Nernst's pupils M. Pier, N. Bjerrum, Siegel, and Budde the knowledge of so-determined temperatures was employed for the calculation of the volumetric heat capacities of the principal di- and tri-atomic molecules as well as of the dissociation constants of steam and carbon dioxide (see *Flame and Combustion in Gases*, chapter xxi [11, 1927]).

The spectral line reversal method was first employed by Kurlbaum [32, 1902–3] and later by Fery [23, 1903]. It consists in illuminating the flame under observation with the salt of an alkali metal. Viewed in a spectrometer bright emission lines of the metal vapour employed (if sodium, the resonance doublet $\lambda\lambda = 0{\cdot}5890\text{–}0{\cdot}5896\mu$) are seen. If a source of continuous radiation (e.g. a hot filament) of known and alterable temperature is placed behind the flame, the lines remain bright so long as the source is cooler than the flame; at higher temperatures the lines are reversed and appear dark upon the bright background of the continuous emission, and the temperature of reversal corresponds with the temperature of the flame.

In recent years a number of papers on the subject have been published by the U.S. Bureau of Mines. In the following table data relating to a number of typical hydrocarbons have been taken from one of them by G. W. Jones, B. Lewis, J. B. Friauf, and G. St. J. Perrott [28, 1931]:

Hydrocarbon	*Observed max. flame temp. ° C.*	*% Combustible in air at max. flame temp.*	*Theoretical mixture*	*Calculated max. flame temp. ° C.*
Ethylene .	1,975	6·65–7·00	6.50	2,072
Propylene .	1,935	4·45–4·90	4·45	2,050
Butylene .	1,930	3·35–3·45	3·35	2,033
Propane .	1,925	4·05–4·30	4·00	1,967
Isobutane .	1,900	3·15–3·25	3·10	1,973
Butane .	1,895	3·15–3·40	3·10	1,973
Ethane .	1,895	5·70–5·95	5·65	1,949
Natural gas	1,890	8·60–9·10	8·60	1,928
Methane .	1,880	9·45–10·10	0·45	1,918

In Fig. 17 the curves for methane, ethane, butane, and ethylene have been selected as showing the variation of flame temperatures with mixture composition. Commenting on these figures the authors came to the following conclusions:

> '1. As would be anticipated, the flame temperature is markedly affected by the proportion of combustible gas

in air. The flame temperature increases rapidly, starting with a mixture near the lower limit of inflammability and reaches a maximum when the mixture contains combustible slightly in excess of that necessary to consume all the oxygen present. The reason for this slight shift from a stoichiometric mixture lies in the dissociation of the products of combustion at the high temperatures developed. This is borne out by the calculated temperatures (dotted lines, Fig. 17) whose maxima, allowing for dissociation, agree well with the observed maxima. With further increases in the percentage of the combustible the flame temperature again decreases but not as sharply as with excess of air. 2. The maximum flame temperatures of the gases tested vary from 1,880° for methane to 1,975° C. for ethylene; the maximum variation among the hydrocarbons is less than 100°. 3. The maximum flame temperatures of the unsaturated hydrocarbons are greater than those of the saturated hydrocarbons. 4. In most cases the maximum flame temperature occurs over a very narrow range of gas/air ratios; a slight change in gas/air ratio at the maximum causes a sharp reduction in the flame temperature.'

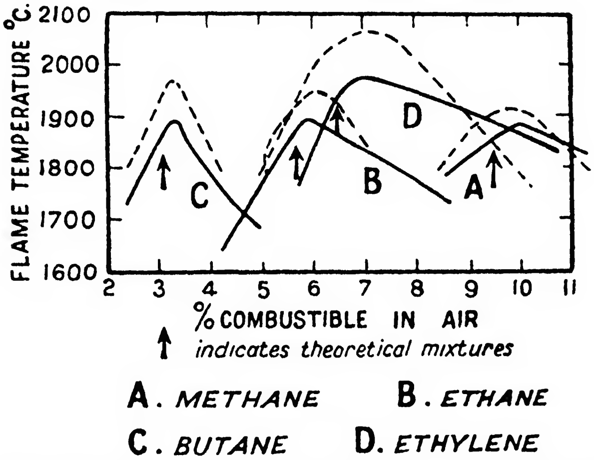


FIG. 17. Flame temperatures of hydrocarbons burning in air (Jones, Lewis, Friauf, and Perrott).

For the method employed and data for heat capacities and dissociation constants used in arriving at the calculated values the original paper should be consulted. Generally the difference between the calculated and observed temperatures was about 100° for the unsaturated and 40–70° for the saturated hydrocarbons (cf. Maxwell and Wheeler's explosion results, p. 2976); the difference being greater the higher the temperature. The authors considered that, assuming the specific heat, &c., data to be reasonably correct, the difference between the values could be attributed to the radiation losses in each particular case.

In a later paper (G. W. Jones, B. Lewis, and H. Seaman [29, 1931]) flame temperatures of the binary mixtures methane-oxygen, methane-hydrogen, and methane-acetylene with air at varying air/gas ratios were determined. Addition of oxygen to methane increased the maximum flame temperature when burned in air; thus with a 20 O_2:80 CH_4 mixture the maximum flame temperature was increased by 5%. When mixtures varying from pure methane to pure hydrogen were burned, as the hydrogen was increased the maximum flame temperature increased only slightly up to about 80% hydrogen, after which it increased rapidly. The flame temperatures of methane-acetylene mixtures with air were determined with mixtures of the two from pure methane to 20% CH_4: 80% C_2H_2; the maximum temperatures for the different mixtures lie almost on a straight line. The addition of small amounts of acetylene to pure methane caused a considerable increase in the flame temperature. It was impossible to determine the flame temperature of pure acetylene in air, but extrapolation indicated a maximum temperature of 2,325° C.

The maximum flame temperatures of all the binary mixtures tested showed that the highest temperatures were reached when oxygen was slightly in defect.

It may here be mentioned that flame temperatures of acetylene-oxygen and hydrogen-oxygen mixtures have also been determined recently by H. H. Lurie and G. W. Sharman [35, 1933] using the same method. Maximum temperatures of 3,400° C. with a 56% O_2: 44% C_2H_2 mixture and 2,930° C. with a 23% O_2: 77% H_2 mixture were recorded.

W. T. David has carried out in recent years [17, 1929–35] an extensive investigation into explosion temperatures mainly of mixtures with air of carbon monoxide and methane, using the platinum resistance method (0·0005-in. platinum-rhodium wire). The temperatures so found were frequently much higher than those calculated from pressure measurements in the same experiments.

He has also expressed the view that flame temperatures determined by the spectral reversal method are sometimes far greater than the true flame temperature (mean molecular translational energy). Thus with carbon monoxide-air mixtures (the data concerning which are more complete than with methane-air mixtures) the spectral method and the platinum resistance method yield very nearly the same temperatures for mixtures approximating to the theoretical; with other mixtures, however, the two methods yield temperatures which differ increasingly until when a 52% CO-air mixture is reached the difference amounts to as much as 400° C. The spectral reversal temperatures measured by Ellis and Morgan [21, 1932] over this wide range of mixture strength remained roughly constant at rather more than 1,900° C., and qualitatively similar results were obtained by Loomis and Perrott [34, 1928] and by Griffiths and Awbery [25, 1929]. The platinum wire temperatures, on the other hand, dropped through this range of mixture strengths by more than 400° C., and this is much more in accord with what would be expected from calculation. An examination of the measurements of Jones, Lewis, and Seaman [29, 1931] of various hydrocarbon-air flames shows that they are also frequently greater than the calculated temperatures, particularly with rich mixtures (cf. curves for ethylene-air mixtures, Fig. 17.

REFERENCES

1. BAEYER, A., and VILLIGER, V. *Ber.* **33**, 3387 (1900); **34**, 738 (1901).
2. BEATTY, H. A., and EDGAR, G. *J.A.C.S.* **56**, 107 (1934).
3. ——— *J.A.C.S.* **56**, 102 (1934).
4. BERKEBUSCH.
5. BLAIR, E. W., and WHEELER, T. S. *J.S.C.I.* **41**, 303 T; **42**, 415 T (1922–3).
6. BONE, W. A. Bakerian Lecture, *Proc. Roy. Soc.* **137**, 243 (1932).
7. BONE, W. A., and ALLUM, R. E. *Proc. Roy. Soc., A*, **134**, 578 (1932).
8. BONE, W. A., and DAVIS, H. *J.C.S.* **105**, 1691 (1914).
9. BONE, W. A., HAFFNER, A. E., and RANCE, H. F. *Proc. Roy. Soc., A*, **143**, 16 (1933).
10. BONE, W. A., and HILL, S. G. *Proc. Roy. Soc., A*, **129**, 434 (1930).
11. BONE, W. A., and TOWNEND, D. T. A. *Flame and Combustion in Gases.* Longmans, Green & Co., 1927.

12. Bowen, E. J., and Tietz, E. L. *J.C.S.* 234 (1930).
13. Brown, G. G., and collaborators. *Ind. Eng. Chem.* **17**, 397 and 1228 (1925); **19**, 280, 363, and 366 (1927); **20**, 1032 (1928); **21**, 1071 and 1261 (1929).
14. Callendar, H. L., and Mardles, E. W. J. *Engineering*, 4 Feb. 1927.
15. Dalton. *New System of Chemical Philosophy*, 1808.
16. David, W. T. *Phil. Mag.* **39**, 84 (1920); **40**, 318 (1920). *Proc. Roy. Soc.*, *A*, **108**, 618 (1925).
17. —— *Engineering*, 2 Nov. 1934. *Nature*, **134**, 663 (1934); **135**, 470 (1935).
18. Duchêne, R. *Chim. et Ind.* June 1933, p. 492. *J. usines gaz.* **55**, 524 (1931).
19. Dumanois, P., Mondain-Monval, P., and Quanquin, B. *Comp. rend. Acad. Sci. Paris*, **191**, 299 (1930).
20. Egerton, A. C. *Nature*, **122**, 19 (17 July 1928); Pidgeon, L. M., and Egerton, A. C., *J.C.S.* 661 (1932).
21. Ellis, O. C. De, and Morgan, E. *Trans. Faraday Soc.* **28**, 826 (1932).
22. Fenning, R. W. *Phil. Trans. Roy. Soc.*, *A*, **22**, 5 (1926); *Rep. and Mem. Aeronautical Research Committee*, no. 979, p. 231 (1925).
23. Fery, C. *Compt. rend.* **137**, 909 (1903).
24. Fort, R., and Hinshelwood, C. N. *Proc. Roy. Soc.*, *A*, **127**, 216 (1930).
25. Griffiths, E., and Awbery, J. H. *Proc. Roy. Soc.*, *A*, **123**, 401 (1929).
26. Haslam, R. T., Lovell, W. G., and Hunneman, R. D. *Ind. Eng. Chem.* **17**, 272 (1925).
27. Helmholtz. See B.A. Reports, 1910; p. 469.
28. Jones, G. W., Lewis, B., Friauf, J. B., and Perrot, G. St. J. *J.A.C.S.* **53**, 869 (1931).
29. Jones, G. W., Lewis, B., and Seaman, H. *J.A.C.S.* **53**, 3992 (1931).
30. Julius. *Die Licht- und Wärmestrahlung verbrannter gase.* Berlin, 1890.
31. Kowalsky, A., Tschirkow, and Sandownikow, P. *Phys. Z. d. Sowjetunion*, **1**, 451 (1932).
32. Kurlbaum, F. *Physik. Z.* **3**, 332 (1902).
33. Lenher, S. *J.A.C.S.* **53**, 2420 and 3737 (1931).
34. Loomis, A. G., and Perrot, G. St. J. *Ind. Eng. Chem.* **20**, 1007 (1928).
35. Lurie, H. H., and Sherman, G. W. *Ind. Eng. Chem.* **25**, 404 (1933).
36. Mardles, E. W. J. *Rep. and Mem. Aeronautical Res. Comm.* no. 1374 (1930); no. 1524 (1933); also *Trans. Faraday Soc.* **27**, 681 (1931).
37. Marvin, C. F., and Best. *National Advisory Comm. for Aeronautics Rep.* no. 399 (1931).
38. Maxwell, G. B., and Wheeler, R. V. *J.C.S.* 1927, p. 2069; 1929, p. 245.
39. —— —— *J.I.P.T.* **14**, 175 (1928); *Ind. Eng. Chem.* **20**, 1041 (1928).
40. Neumann, K., and Andrejew. *J. Phys. Chem.* (Russ.), **4**, 33 (1933).
41. Neumann, K., and Egorow. *Phys. Z. d. Sowjetunion*, **1**, 536 (1932).
42. Neumann, K., and Serbinoff, A. *J. Phys. Chem.* (Russ.), **4**, 41 (1933).
43. Newitt, D. M., and Block, A. M. *Proc. Roy. Soc.*, *A*, **140**, 426 (1932).
43*a*. Newitt, D. M., and Gardner. *Proc. Roy. Soc.*, *A*, **154**, 329 (1936).
44. Newitt, D. M., and Haffner, A. E. *Proc. Roy. Soc.*, *A*, **134**, 591 (1932).
45. Newitt, D. M., and Szego, P. *Proc. Roy. Soc.*, *A*, **147**, 555 (1934).
46. Norrish, R. W. *Proc. Roy. Soc.*, *A*, **150**, 36 (1935).
47. Paschen. *Ann. Phys. Chem.* **52**, 214 (1894).
48. Pease, R. N. *J.A.C.S.* **51**, 1839 (1929).
49. Pease, R. N., and Munro, W. P. *J.A.C.S.* **56**, 2034 (1934).
50. Pope, J. C., Dykstra, F. J., and Edgar, G. *J.A.C.S.* **51**, 1875 and 2203 (1929).
51. Prettre, M. Theses, University of Paris, 1931.
52. Semenoff, N. *Chemical Kinetics and Chain Reactions.* Clarendon Press, 1935.
53. Spence, R., and Kistiakowsky, G. B. *J.A.C.S.* **52**, 4837 (1930).
54. Thompson, H. W., and Hinshelwood, C. N. *Proc. Roy. Soc.*, *A*, **125**, 277 (1929).
55. Tizard, H. T., and Pye, D. R. *Rep. Empire Motor Fuel Committee*, 1924.
56. Waggener. *Ves. deut. physik. Ges.* **14**, 78 (1895).
57. Wheeler, R. V. *J.C.S.* **113**, 45 (1918).
58. White, A. G. *J.C.S.* **125**, 2387 (1924).
59. —— *J.C.S.* **121**, 1244, 1688, and 256 (1922).
60. Withrow, L., and Boyd, T. A. *Ind. Eng. Chem.* **23**, 539 (1931).

COMBUSTION PHENOMENA AT HIGH PRESSURES

By D. M. NEWITT, D.Sc., and D. T. A. TOWNEND, D.Sc.

Imperial College of Science and Technology

One of the achievements in chemical technology in recent years has been the development of processes and plant for the utilization of high pressure in industrial operations, and mention need only be made of new pressure processes for the synthesis of methyl alcohol, the hydrogenation of coal, and the cracking of petroleum oils to indicate the extent of its use and the important results it has accomplished. It is proposed in this section to describe some of its applications to combustion processes and more particularly to those in which hydrocarbons undergo homogeneous oxidation in the vapour phase.

Before doing so, however, it will be well to enumerate briefly some of the more important effects which pressure may be expected to exert upon the course of such reactions. In accordance with the van't Hoff principle of mobile equilibrium, increase of pressure will favour transformations which occur with a diminution in volume and will hinder those which involve an increase. As a consequence there will be a tendency for reactions involving dissociation or thermal decomposition to be suppressed. Pressure will also increase the absolute amount of chemical change in a system by proportionately increasing the frequency of the molecular collisions; and, in the case of chain reactions, it may increase the velocity by delaying chains reaching the walls of the reaction vessel. Other effects associated with radiation phenomena will be mentioned later. We may therefore anticipate that, whilst the main course of a combustion will not be materially altered by increasing pressure, the relative proportions of intermediate compounds surviving may change considerably, and secondary reactions resulting in 'condensations' may also occur.

Although there is a considerable patent literature dealing with slow combustion at high pressures and relating mainly to the selective influence of catalysts, it is only recently that data upon the homogeneous reaction of the simpler hydrocarbons with oxygen have been published. Newitt and collaborators in England have worked with methane, ethane, and some of the aromatic hydrocarbons [11, 1932; 12, 1932; 13, 1933], whilst Frolich and collaborators [16, 1934] in America have confined their attention more particularly to 'natural' gas and the higher paraffin hydrocarbons.

In the investigations referred to, both static and flow methods have been employed with a view to ascertaining *inter alia* the optimum conditions for the isolation in quantity of intermediate oxygenated products. Owing to the highly exothermic character of the reactions involved, provision has always to be made for dissipating the heat liberated so that large increases in temperature may be avoided. In small-scale experiments this is usually done by diluting the reacting media either with excess of the combustible or with some inert gas, and most of the data available have been obtained with mixtures containing not more than about 20% of oxygen. A brief account will now be given of some of the more important results.

Methane.

Newitt and Haffner [12, 1932] have studied the slow combustion of methane at pressures up to 150 atm., and find that whilst in general the characteristic features of the low-pressure oxidation are maintained, there are considerable changes in the relative proportions of the various intermediate compounds surviving in the products.

As a typical example we may consider the case of an $89CH_4/11O_2$ mixture at 106 atm. undergoing reaction in a steel vessel heated to 339° C. On admitting such a mixture to the previously heated vessel there is an induction period of some 14 min. during which no detectable combination takes place, followed by a reaction period of 22 min. during which all the available oxygen is used up. Analysis of samples taken at periodic intervals during the experiment shows that both methyl alcohol and formaldehyde are present in traces towards the end of the induction period and gradually accumulate in the system, but whereas the concentration of the alcohol continues to increase as long as any free oxygen remains, that of the formaldehyde reaches a maximum when reaction is about two-thirds complete and thereafter diminishes. The two oxides of carbon and steam are found at an early stage and accumulate in the system as reaction proceeds.

On increasing the reaction temperature, pressure being maintained constant, both the induction and reaction periods progressively decrease until eventually at a sufficiently high temperature instantaneous ignition occurs, accompanied by copious carbon deposition. The amounts of alcohol and formaldehyde surviving in the products at first increase with reaction velocity, reach a maximum value, and then diminish, as shown by the following figures:

Reaction temperature, ° C.	*Products as percentage of methane burnt*		*Ratio CO/CO_2 in gaseous products*
	CH_3OH	H·CHO	
336	10·1	0·30	0·05
339	14·1	0·36	0·01
341	22·3	0·75	1·5
343	20·0	0·93	1·0
352	9·8	0·95	3·9
355	3·8	traces	4·2

Under the given experimental conditions, therefore, there would appear to be an optimum rate of reaction favourable to the survival of intermediate products.

The effect of increase of pressure in altering the relative proportion of the products is shown by the data given in Table I. It should be noted that at each pressure the reaction temperature has been chosen with a view to giving the optimum reaction velocity for their survival. In these circumstances the amount of methyl alcohol found increases progressively with pressure, whilst the corresponding figure for formaldehyde shows a tendency towards a maximum value at about 40 atm.

By carrying out pressure oxidations in a flow system and regulating the rate of flow through the heated zone, oxidation can be partially arrested at an early stage and the initially formed products isolated in quantity [14, 1934]. In this way it has been found that with a very dilute mixture ($CH_4 = 90$, $O_2 = 3$, $N_2 = 7$) at 50 atm. and 430° C. as much as 51% of the methane burnt is recoverable in the

TABLE I

The Effect of Pressure upon the Survival of Methyl Alcohol and Formaldehyde in the Products of the Oxidation of an $8{\cdot}1CH_4+O_2$ *Medium (Newitt and Haffner)*

Initial pressure, atm.	*Reaction temperature, ° C.*	*Products as percentage of methane burnt*		*Ratio* CO/CO_2 *in gaseous products*
		CH_3OH	$H{\cdot}CHO$	
10	400	1·1	nil	0·06
25	385	4·8	0·66	0·15
40	372	6·1	1·20	0·05
48	373	13·7	0·8	0·35
106·4	341	22·3	0·75	. .
149	341	19·0	0·60	0·08

products as methyl alcohol. The effect of altering the rate of flow whilst maintaining the pressure and temperature approximately constant is shown by the following data:

Initial mixture	*Reaction temperature, ° C.*	*Duration of heating, sec.*	*Percentage of methane burnt surviving as*	
			CH_3OH	$H{\cdot}CHO$
$CH_4 = 90$	435	5	51	4·1
$O_2 = 3$	435	7	49	3·2
$N_2 = 7$	425	10	43	3·2
	428	20	12	2·2

It is important to note that the ratio $CH_3OH{:}H{\cdot}CHO$ increases with the velocity, a result that lends support to the view that methyl alcohol is the initial product of the oxidation. In applying the flow method on an industrial scale it would probably be necessary to use a circulating system in which the condensable products would be renewed during each cycle and sufficient oxygen (or oxygen-containing gas) and hydrocarbons added to compensate for that used up. The disadvantage of the method is the gradual dilution of the reacting mixture with the gaseous products of combustion and other inert gases and the consequent falling off in yield. As an indication of the effect of diluents a comparative series of oxidations in which a $2CH_4+O_2$ mixture was diluted with (*a*) excess of the combustible, (*b*) excess of one of the products of combustion, steam or carbon dioxide, and (*c*) excess of nitrogen, the total pressure of the reacting medium being 50 atm., gave the following results:

Initial mixture $2CH_4+O_2$ *plus*	*Reaction temperature, ° C.*	*Time of reaction, min.*	*Amounts of* CH_3OH *and* $H{\cdot}CHO$ *surviving in products; c.c. at N.T.P.*	
			CH_3OH	$H{\cdot}CHO$
$6{\cdot}5\ CH_4$	397	1	80	4·6
$6{\cdot}5\ CO_2$	390	8	50	3·0
$6{\cdot}5\ H_2O$	400	2	43	1·6
$6{\cdot}5\ N_2$	397	16	48	2·7

The action of the inert diluents is generally to slow down the rate of reaction, nitrogen being the most effective, and also to diminish the amounts of methyl alcohol and formaldehyde surviving.

Ethane.

The data relating to methane as representative of the paraffin hydrocarbons has been given in some detail. Ethane shows similar characteristics, although its combustion involves a greater number of intermediate stages and a more complex series of products. It oxidizes with greater ease than does methane, giving alcohols, aldehydes, acids, steam, and the two oxides of carbon in proportions which vary both with pressure and temperature [11, 1932].

As with methane, there appears to be an optimum rate of reaction for the survival of the initially formed products (alcohols, aldehydes, and acids). Thus with an $88C_2H_6/12O_2$ mixture at 100 atm. pressure the effect of increasing the reaction temperature from 262·2°, at which combination takes place comparatively slowly, to 278·0° is shown by the data in Table II.

Attention may be drawn to certain features of these results which are of interest in connexion with the mechanism of the combustion. According to the hydroxylation theory, the initial stages of oxidation follow the sequence

$$CH_3{\cdot}CH_3 \rightarrow CH_3{\cdot}CH_2OH \rightarrow CH_3CHO \rightarrow CH_3COOH.$$

The survival of comparatively large quantities of acetic acid in the products from low-temperature oxidations would suggest that it is more resistant to oxidation than is acetaldehyde and therefore tends to accumulate in the system. At higher temperatures the rate of thermal decomposition of acetaldehyde would appear to exceed that of its oxidation to the acid, with the result that the concentration of the latter diminishes and the products of the decomposition of the aldehyde (methane and carbon monoxide) appears in increasing quantities. As the stability of the aldehyde would presumably be increased by pressure, the conditions favourable to the production of acid should be high pressure and comparatively low reaction rates.

The effect of pressure upon the relative proportion of the various intermediate products surviving is shown by the data contained in Table III. It should be noted that the temperatures of reaction have been progressively lowered with increasing pressure, so that the rates of reaction are approximately constant throughout.

On carrying out the reaction by a continuous flow method [14, 1934] in such wise that the reaction medium is subjected to heat for a short period only and is immediately cooled, it is possible partially to arrest the oxidation so that the initial products are found in large quantities. Thus when a $C_2H_6 = 90$, $O_2 = 3$, $N_2 = 7\%$ mixture at 50 atm. pressure is passed through a tube heated to 360° C. at such

TABLE II

Reaction Products of an $88\ C_2H_6/12\ O_2$ *Medium at 100 Atm. and Temperature between 262·2 and 278·0° C.*

Initial temp., ° C.	*Duration of*		*Percentage of the carbon of the ethane burnt appearing as*									*Total carbon so accounted for, %*
	Induction, min.	*Reaction, min.*	C_2H_5OH	CH_3OH	CH_3CHO	$H{\cdot}CHO$	CH_3COOH	$H{\cdot}COOH$	CO	CO_2	CH_4	
262·2	25·0	15·0	22·6	10·5	6·2	0·04	27·2	0·8	8·9	19·2	2·0	97·44
265·0	21·0	13·0	21·8	12·5	6·6	0·08	22·4	0·7	18·8	15·9	1·1	99·88
266·5	23·5	11·0	23·7	11·2	6·0	0·05	23·8	0·6	9·3	14·2	8·6	97·45
270·5	12·0	4·5	23·6	14·0	9·7	0·05	12·5	0·5	22·4	8·7	8·6	100·05
275·0	5·75	2·75	16·5	13·1	6·8	0·10	4·9	0·3	37·2	5·1	16·1	100·10
278·0	4·0	1·25	14·6	15·4	11·1	0·60	2·2	0·3	37·6	2·8	14·3	98·90

TABLE III

The Effect of Initial Pressure on the Survival of Intermediate Products from the Reaction of an $88{\cdot}4C_2H_6/11{\cdot}6O_2$ *Medium (Newitt and Bloch)*

Initial pressure, atm.	*Reac. temp., °C.*	*Duration of reac., min.*	*Percentage of the carbon of the ethane burnt surviving as*						*Total condensable products, %*
			C_2H_5OH	CH_3OH	CH_3CHO	$H\cdot CHO$	CH_3COOH	$H\cdot COOH$	
15	315	3·0	16·0	19·4	1·9	4·5	nil	nil	41·8
50	294	3·25	17·2	14·1	5·2	1·9	nil	0·7	39·1
75	279	2·5	18·0	16·6	6·8	0·4	3·6	0·6	46·0
100	270·5	4·5	23·6	14·0	9·7	0·1	12·5	0·5	50·4

a rate that the duration of heating is only 4 sec., the composition of the products expressed as percentages of the carbon of the ethane burnt is as follows:

$$C_2H_5OH = 62{\cdot}6,\ CH_3CHO = 4{\cdot}8,\ CH_3COOH = 1{\cdot}1,$$
$$CH_4 = 9{\cdot}3,\ CO = 9{\cdot}2,\ CO_2 = 4{\cdot}7\%.$$

In this experiment about three-quarters of the ethane burnt appears in the products as ethyl alcohol, acetaldehyde, and the product of the thermal decomposition of the aldehyde.

Propane, Butane, Pentane, &c.

Although similar detailed results for the higher paraffins are not available, Wiezerich and Frolich [16, 1934] have published an account of work on a semi-commercial scale, together with relevant data relating to control laboratory experiments with propane, butane, and pentane.

They find the principal condensable products of pressure oxidation are alcohols, aldehydes, and acids in proportions depending upon pressure, temperature, and time of heating. Thus in the case of *n*-butane-air/or oxygen mixtures containing 6·2 mols % of oxygen, the following results were obtained:

Oxidizing gas	*Air*	*Oxygen*
Mols % of oxygen in inlet gas	6·2	6·4
Pressure, atm.	160	140
Reaction temperature, ° C.	410	281
Percentage of oxygen converted to alcohols (methyl, ethyl, propyl; ratio about 1 : 2 : 3)	21·9	18·6
Butyl alcohol	1·5	1·0
Acetic acid	8·7	11·2
Aldehydes	6·1	16·4
Water	18·5	21·0
Gaseous products	37·8	29·5

By varying the pressure it was found that low pressure favoured the survival of the lower alcohols and acids, and high pressures the higher alcohols and aldehyde.

Attempts were also made to obtain increased yields of acids by employing a circulatory system, in which the acids were removed during each cycle, and the remaining products, together with the unchanged hydrocarbon, recirculated. In one such experiment liquid propane (containing 3–7% of ethane and 3–7% of higher hydrocarbons) was saturated with air at 133 atm. and was then passed successively through a preheater maintained at 175° C. and a reactor immersed in a lead bath at 400° C. From the reactor the products passed through a system of condensers and separators in which the acid and permanent gases were removed, the remaining products and unchanged propane being returned to the air saturator.

The yields, expressed in litres per 1,000 litres of propane per pass, were as follows:

	Litres
Acetic acid	1·5
Formic acid	1·1
Intermediate products remaining in system after run	8·0
Formaldehyde	0·4
Propane lost as CO_2 and CO	7·0
Water	9·5

At the end of 3·3 days of continuous operation the propane contained only 7% of non-acidic products. About 80% of the total intermediate products remained undissolved in the propane and consisted mainly of methyl and ethyl alcohols and acetone. Of the total acids made, 46% by volume was formic acid, whilst acids higher than acetic acid increased from 9% by volume of total acids to above 14% towards the end of the run.

There is little or no evidence to show that catalysts have any selective action in respect of the intermediate reactions occurring during the combustion of the paraffins. The known oxidation catalysts in most cases carry combustion through to the later stages where gaseous products predominate, or they accelerate the thermal decomposition of intermediate products with the same result. Whilst, therefore, the possible advantages arising from a suitably catalysed combustion must not be overlooked, experimental evidence so far indicates that quite satisfactory results may be obtained without their intervention.

Slow Combustion of the Aromatic Hydrocarbons

With the exception of benzene, the homogeneous slow combustion of the aromatic hydrocarbons has not been extensively investigated. In general, however, reaction appears to proceed by a 'chain' mechanism [9, 1930], and during the initial stages oxygen enters both the nucleus and the side-chains, giving rise in the former case to phenolic compounds, and in the latter to aromatic alcohols, aldehydes, and acids. As combustion proceeds a point is reached at which the ring structure breaks, giving a complex series of products including maleic acid, formic acid, the oxides of carbon and steam.

Benzene.

At atmospheric pressure benzene reacts with oxygen at a conveniently measurable rate at temperatures of about 500° C., the final products consisting principally of the two oxides of carbon and steam and a small residue of methane [9, 1930]. In a silica or porcelain vessel the reaction is predominantly homogeneous, its rate varying according to a high power of the benzene concentration. When the benzene-oxygen mixture is first admitted to the reaction vessel there is an interval during which the pressure increases only very slowly, although oxygen is being used up and carbon monoxide formed. This cannot be regarded as a true induction period, but probably results from the formation with contraction in volume of some intermediate oxygenated product sufficient in quantity to compensate for the rise of pressure accompanying the formation of oxides of carbon. It is succeeded by a period of rapid pressure rise, during which reaction proceeds to completion.

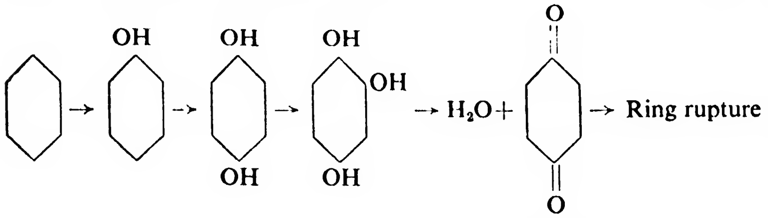
For a given ratio of benzene to oxygen the rate of oxidation increases rapidly with the pressure. Thus Fort and Hinshelwood [9, 1930] find that for a $C_6H_6/O_2 = 1/3$ mixture the times for the pressure to increase from 20 to 60% of the total increase corresponding to complete reaction are as follows:

Total pressure, mm.	*Times for increase from 20 to 60%, min.*
400	5·5
300	9·6
200	38·4

The 'order of reaction' calculated from these figures varies from 3 to upwards of 4; and since it cannot be supposed that three or four molecule collisions are necessary for reaction, the probability is that a chain mechanism is involved.

At high pressures oxidation proceeds smoothly with no induction period and, provided the temperature is controlled, with no liberation of carbon or tar formation. In the absence of catalysts the principal products are phenol, the oxides of carbon and steam, together with traces of hydroquinone, quinone, maleic acid, and formaldehyde.

Some rupture of the ring always occurs, although in certain circumstances the greater part of the oxygen used survives as phenol and other hydroxy compounds. It would appear from a consideration of the available data that the earlier stages of the process involves successive hydroxylations, somewhat as follows:



The conditions most favourable to the survival of these products, and in particular of phenol, are (*a*) a reacting medium containing a large excess of the hydrocarbon, (*b*) a pressure of 50 atm. and upwards, and (*c*) a temperature sufficiently high to give rapid but flameless combustion. Thus, for example, with a $40C_6H_6/10$ air mixture at 50 atm., reacting in a closed steel vessel at 370° C., 53·3% of the benzene oxidized was recovered as phenol, the balance consisting largely of the oxides of carbon.

Toluene.

The presence of a side-chain in the nucleus facilitates oxidation, but also gives rise to complications due to its simultaneous oxidation with the nucleus. Thus in the case of toluene Newitt and Szego [13, 1933] have found that benzyl alcohol, benzaldehyde, and benzoic acid are formed as the result of side-chain oxidations, together with 2·4 dihydroxy toluene and other aromatic hydroxy derivatives.

Toluene differs from benzene in that there is a well-defined induction period preceding reaction and it is easier to control the subsequent oxidation so as to produce considerable quantities of one or other of the intermediate products. High pressure, together with excess of the hydrocarbon, for example, is found to favour the survival of the alcohol, whilst a progressive increase in the oxygen concentration causes the reaction to proceed at first mainly to the aldehyde stage and then to benzoic acid. By careful control it is found possible, even in a static system, to obtain yields of aromatic derivatives representing upwards of 70% of the toluene consumed.

The foregoing account will perhaps suffice to indicate some of the potential applications of pressure oxidation. Of the hydrocarbons specifically mentioned, the paraffins occur in vast quantity in 'natural gas', in the gases evolved during oil-cracking, and in the products of the anaerobic fermentation of sewage sludge; to a large extent they are now considered a waste product or are utilized uneconomically as fuel for power-raising purposes.

In some few instances large-scale oxidation processes are in operation, but generally speaking the technical difficulties involved have hindered development [16, 1934]. It will be apparent from the work described that the problem is essentially one of adequate temperature control, for the reactions involved are generally highly exothermic and large quantities of heat have to be removed by suitable heat exchange or otherwise. On the other hand, a well-balanced plant should be practically self-supporting, the heat evolved providing all the power requirements of the process.

Explosion Phenomena at High Pressures

The influences operative in high-pressure explosions may be summarized as follows [3, 1930]:

(1) An increase in the density of an explosive medium generally increases the absolute amount of chemical change in a given volume per second on explosion; and, if such increased rate of combustion is proportionately greater than the increased density of the medium, the 'explosion time' for any particular enclosure is diminished. Such is the usual, though not the invariable, effect for initial pressures up to 200 atm., carbon monoxide-air explosions being notable exceptions.

(2) For any given enclosure the relative heat losses become less, and consequently the maximum temperature becomes greater, as the density of the medium increases.

(3) While pressure by itself diminishes 'dissociation' in any particular case, an increase in the maximum temperature consequent upon higher pressure has an opposite effect, so that what is actually observed is the resultant of the two effects. In carbon monoxide-air explosions the two effects seem hardly to balance, but in hydrogen-air explosions the pressure outweighs the temperature effect.

(4) So far as our present knowledge extends, an increase of pressure generally widens the limits of explosion of a given combustible gas and air mixture, carbon monoxide again being a notable exception.

(5) An increase in the density of the medium may affect both the emission and absorption of radiant energy during an explosion; and as radiation is known to play an important role in 'activating' or 'exciting' molecules, reactions may become prominent in high-pressure explosions which are hardly noticeable at lower pressures.

The Effect of Pressure upon the Limits of Inflammability

In so far as pressure may influence the rate of reaction of a combustible gas-air or oxygen medium and/or the rate at which heat is transmitted through such medium by conduction, convection, or radiation, it will constitute one of the factors determining the limits of inflammability. The magnitude of its effect is found to vary considerably with the nature of the combustible gas, but in general the upper limit is widened by increase of pressure, whilst the lower limit is not much affected. The actual experimental values depend to such an extent upon the method of ignition, the shape and size of the vessel employed, and the direction of flame propagation that close agreement between the results of different experimenters can hardly be expected. It will nevertheless be useful to tabulate such data as is available in some typical instance with a view to contrasting the behaviour of a few representative gases and vapours.

Hydrogen in Air.

Two independent series of observations have been made with the gas. Berl and Werner [2, 1927] determined the limits for downward propagation in a cylindrical steel vessel, ignition being effected by means of an electric spark, with the following results:

Pressure, atm.	*Percentage* H_2 *in limit mixture**	
	Lower	*Upper*
1	6·0	59·0
20	9·0	65·0
40	10·7	67·2
60	9·5	71·0
100	8·8	72·5
200	8·4	74·0

* Values taken from published curves.

Bone, Newitt, and Smith [5–6, 1928] measured the limits for horizontal propagation (*a*) in a cylindrical steel vessel 42 in. long and 2 in. diameter, and (*b*) a spherical steel bomb 3 in. in diameter. The mixtures were ignited by means of a heated platinum wire and the limits were determined by direct observation of the flame (at the lower pressures) or by chemical analysis of the products of combustion. The values obtained are tabulated below:

Pressure, atm.	*Percentage* H_2 *in limit mixture*	
	Lower	*Upper*
1	9·9	. .
5	9·9	68·4
10	10·0+	68·5+
30	10·0+	71·9
50	10·0	73·3
75	9·9	74·2+
125	9·9	74·8+

The + sign denotes that the figure in question is probably fractionally lower than the true value.

It will be noticed that in both series there is a slight tendency for the hydrogen content of the lower limit mixtures to reach a maximum between about 10 and 40 atm., although the range of inflammability increases with pressure throughout. The same effect is observed with other gases and is particularly marked with hydrocarbons.

Carbon Monoxide in Air.

Carbon monoxide presents an unusual feature in that the range of inflammability in air contracts with increasing pressure in such a way as to suggest that at a sufficiently high pressure combustion would not take place at all. Thus between 1 and 125 atm. there is a contraction of upwards of 45%. The following values are for horizontal propagation in a spherical steel vessel 3 in. in diameter.

Pressure, atm.	*Percentage* CO *in limit mixture*	
	Lower	*Upper*
1	14·2	71·0
5	15·4	67·5
10	17·8	62·8
30	20·3	58·8
50	20·6	56·8
125	20·7	51·6

A similar effect is found when the nitrogen of the air is replaced by an inert gas such as argon or helium. Thus with 'argon-air' the values at 10 and 50 atm. are:

Pressure, atm.	*Percentage* CO *in limit mixture*	
	Lower	*Upper*
10·0	14·0	66·0
50·0	15·3	60·4

The reason for this unusual behaviour has been traced in part to the progressive diminution in humidity of the reacting medium with increase of pressure; for, as is well known, the rate of slow combustion of carbon monoxide is very sensitive to the hygroscopic state of the medium, and any alteration might well produce a considerable effect, particularly in view of the critical conditions which prevail at the limit.

When experiments are carried out under such conditions that the humidity of the medium can be maintained at some constant high value, it is found that the range of inflammability is almost independent of pressure. Thus with carbon monoxide-air mixtures, 80% saturated at 100° C., the following values for the limits were found (Bone, Newitt, and Smith [6, 1928]):

Pressure, atm.	*Hygroscopic condition of mixture*	*Percentage* CO *in limit mixture*		*Range of inflammability* $(U-L)$
		Lower	*Upper*	
32·2	'Dry' and at 100° C.	18·1	62·7	44·6
	80% saturated at 100° C.	15·7	65·7	60·0
64·4	'Dry' and at 100° C.	18·9	59·3	40·4
	80% saturated at 100° C.	16·6	66·7	50·1

It can be seen that not only is the range of inflammability for a constant humidity condition unaffected by pressure, but that the limits at any particular pressure widen with increase of humidity.

Methane in Air.

The curves in Fig. 1 showing the variation of the upper and lower limits of downward propagation with pressure present several features of interest [1, 1929]. In the first place it should be noted that for certain weak hydrocarbon-air mixtures there are two lower limits. Thus, for example,

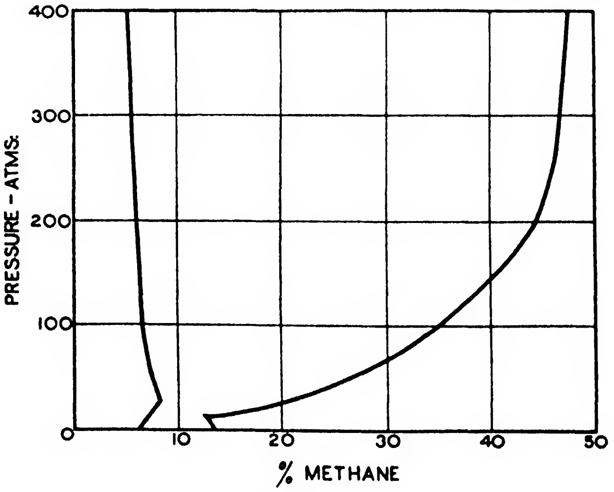


FIG. 1.

a 7·5% methane mixture would propagate flame below 25 and above 50 atm., but not at intervening pressures. A similar, but not so marked, effect occurs at the upper limit. The upper limit also shows a remarkable variation with pressure increasing from 13% at atmospheric pressure to 47%, approximately, at 400 atm.

For horizontal propagation in a 3-in. steel sphere a similar general widening of the explosion range is observed, although the evidence for the existence of two lower and upper limits for certain mixtures is not decisive. Below are given values for the limits between 1 and 125 atm.:

Pressure, atm.	*Percentage methane in limit mixture*	
	Lower	*Upper*
1	5·6	14·3
5	5·7	16·4
10	6·0	17·1+
30	5·9	24·6+
50	5·4	29·0+
125	5·7	45·5+

Ethylene in Air.

Ethylene behaves in a similar way to methane, the range of inflammability increasing with pressure, particularly as regards the upper limit [1, 1929]. Also, for certain weak mixtures containing between 2·5 and 6% of ethylene, approximately, there are two distinct limits defined by the pressure of the system. The data for downward propagation in a cylindrical steel vessel are as follows:

Pressure, atm.	*Percentage ethylene in limit mixture**	
	Lower	*Upper*
1	2·5	14·0
10	4·0	28·0
25	6·0	48·0
80	3·9	62·0
160	1·8	69·5
320	1·0	70·5

* Read from published curves.

Liquid Hydrocarbons in Air.

The limits of explosion for the higher (liquid) hydrocarbon-air mixtures depend not only upon the temperature and total pressure of the system, but also upon the vapour pressure of the combustible [1, 1929]. If, for example, the total pressures and temperatures corresponding to limiting saturated hydrocarbon-air mixtures are plotted graphically, two curves similar to those illustrated in Fig. 2 (which relate to benzene-air mixtures) are obtained. They show, *inter alia*, that at low temperatures the effect of increasing the total pressure is so to alter the composition of the medium as to give an upper and lower limit mixture within a comparatively small pressure range. At high temperatures, on the other hand, the vapour pressure of the combustible is so large that whilst the upper limit can easily be determined, it requires exceedingly high pressures to reach the lower limit.

To express the limits in terms of the hydrocarbon content of the mixture and the pressure a diagram such as Fig. 3 is required. In it are shown (*a*) the saturation curves for benzene vapour in air at various temperatures and pressures, and (*b*) two curves giving the upper and lower limits as derived from the curves in Fig. 2.

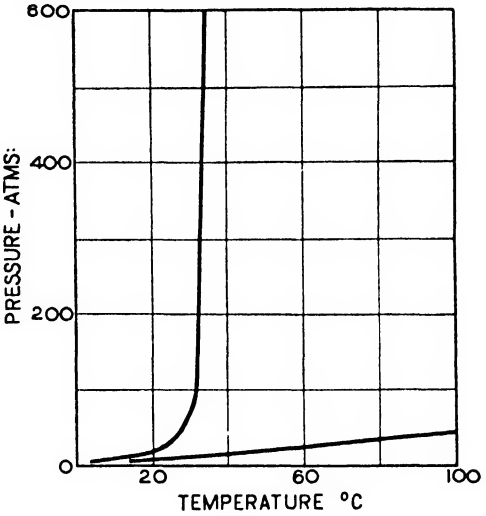


FIG. 2.

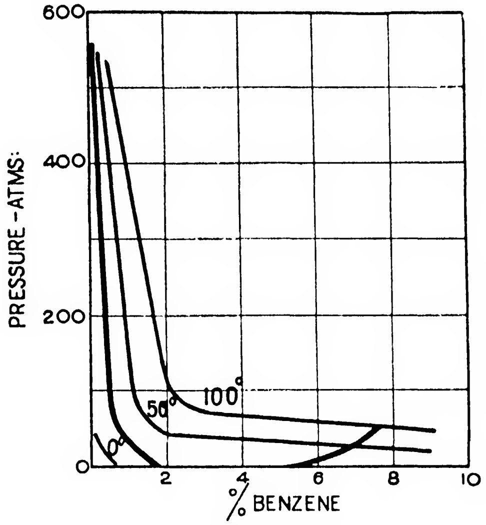


FIG. 3.

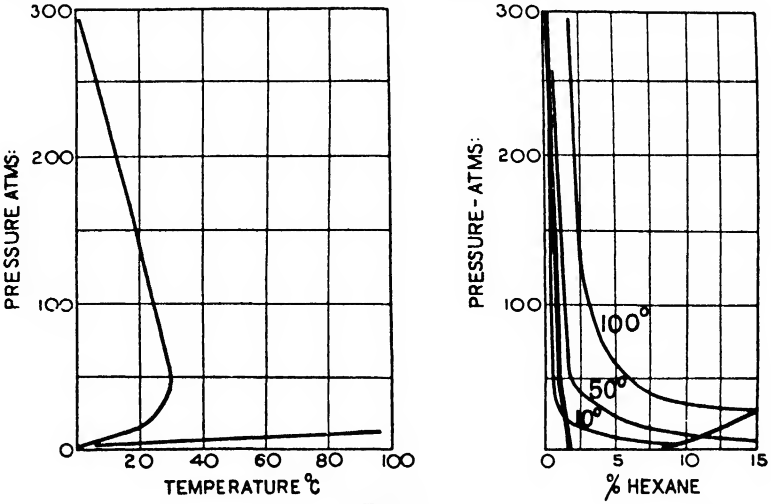


FIG. 4.

At any given temperature, therefore, the range of inflammability is defined by the two limit curves and the corresponding saturated vapour curve.

The higher (liquid) paraffin hydrocarbons, whilst exhibiting the same general behaviour as benzene, differ from it in that at low temperatures there are two pressure limits. Thus in the case of hexane (Fig. 4) a saturated hexane-air mixture at 20° C. would propagate flame between 1 and 10 atm. approximately, and above 130 atm., but not at intervening pressures. The explanation of this phenomenon is not at present clear, although it would appear to be related in some way to the changes in the spontaneous ignition temperature of the hydrocarbons with pressure (see Ignition Temperature with Special Reference, &c.).

The Effect of Pressure upon the Explosion of Theoretical Hydrogen-air and Carbon Monoxide-air Mixtures

When comparatively rich combustible-gas-air mixtures at high initial pressures are exploded in a closed vessel the resulting combination of high temperature and pressure gives rise to phenomena of considerable interest. The progress of such explosions is usually followed by continuous pressure-time records which afford information as to the rate of reaction and the distribution of energy both during explosion and the subsequent cooling period; it is also possible to calculate therefrom the maximum temperatures attained, the extent of dissociation of the gases at maximum pressure, and (on certain assumptions) the mean molecular heat capacities of the individual gases present.

In analysing the records, however, certain 'corrections' incident to the use of pressure have to be applied to the experimental data. These may be summarized as follows [7, 1929]: (i) the observed initial pressure of the explosive mixture (P_i), the maximum explosion pressure (P_m), and the pressure of the cold products (P_f) require a 'compressibility' correction for deviations from the gas laws; (ii) whenever the time for the attainment of maximum pressure (t_m) exceeds about 0·005 sec. a cooling correction is applied to P_m to compensate for the loss of heat by radiation, combustion, and convection during the explosion period; (iii) in calculating the maximum temperature actually attained in an explosion (T_m), due allowance must be made for the change in the number of molecules in the medium at P_m as compared with P_i. If P_{mb} and P_{ib} denote the values of the maximum and initial pressures respectively, corrected for deviation from the gas laws, m the number of molecules present before explosion, and n the number at maximum pressure, then the mean maximum temperature attained during the explosion will be given by

$$T_m = T_i \times \frac{P_{mb}}{P_{ib}} \times \frac{m}{n},$$

where T_i is the initial temperature of the explosive medium.

In the course of a comprehensive investigation into the effect of pressure upon gaseous explosions generally, Bone, Newitt, and Townend have dealt at length with the methods of applying these corrections to the observed experimental results [7, 1929], and reference should be made to their papers for further particulars. They also describe suitable types of equipment and recording instruments for carrying out such experiments; briefly, the apparatus consists of (*a*) a filling system by means of which the component gases of the explosive mixture can be separately introduced in the desired proportions into (*b*) a strong steel bomb fitted with inlet valve, ignition plug, and pressure manometer, and (*c*) an optical system for recording continuously the readings of the manometer.

The explosion bombs used by them for experiments at initial pressures below 200 atm. were spherical in shape and 3 in. in diameter; for pressures above 200 atm. a bomb of special construction, having a cylindrical explosion cavity 3 in. long and 1·5 in. in diameter, was employed. Ignition was always effected by means of a heated platinum wire, and pressure-time records were obtained by an optically recording Petavel manometer. A brief summary of their more important results will now be given.

Hydrogen-air and Carbon Monoxide-air Explosions.

In Fig. 5 are shown typical pressure-time records for the explosion of $2H_2+O_2+4N_2$ and $2CO+O_2+4N_2$ mixtures at initial pressures of 50 atm., which may serve to illustrate the marked difference in the behaviour of the two combustible gases [7, 1929]. In the case of hydrogen there is an almost instantaneous rise (in about 0·005 sec.) to the maximum pressure of about 403 atm., succeeded by a pressure fall during which the pressure-time record assumes the character of a simple cooling curve; after 1 sec. the pressure has decreased by as much as 225 atm. With carbon monoxide, on the other hand, the pressure rises much more slowly and only attains a maximum (about 409 atm.) after 0·19 sec.; it maintains this maximum pressure for a considerable time, after which it falls slowly, the loss of pressure in 1 sec. after the maximum being only 93 atm.

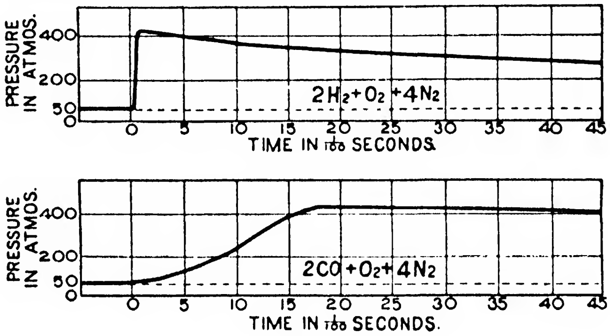


FIG. 5.

In Table IV are given data for a $2H_2+O_2+4N_2$ mixture exploded at initial pressures between 3 and 175 atm. The results show that whilst increase of pressure has little in-

TABLE IV

The Influence of Varying Initial Pressures upon the Explosion of a $2H_2+O_2+4N_2$ *Mixture*

Initial pressure (P_i), atm.	3	10	50	100	150	175
P_i corrected for compressibility (P_{ib}), atm.	2·99	9·95	49·6	98·0	143·5	164·5
Time for attainment of maximum pressure (t_m), sec.	In all cases 0·005 sec. (or less) tending to diminish as P_i increases.					
Maximum pressure (P_m), atm.	23	78	403	850	1,300	1,540
P_m corrected for compressibility (P_{mb}), atm.	23	77·5	391	800	1,185	1,382
Dissociation of steam at P_m, % . . .	2·2	1·8	1·4	1·5	1·2	1·0
Pressure fall in 1 sec. after P_m, % . .	78·3	70·5	55·8	57·0	48·4	40·3
P_{mb}/P_{ib} . . .	7·70	7·79	7·89	8·16	8·26	8·40
T_m, ° C. abs. . .	2,585	2,620	2,665	2,745	2,780	2,825

fluence in the explosion time (t_m), it increases both the ratio P_{mb}/P_{ib} and the maximum temperature (T_m). The dissociation of steam at the maximum is only 2·2% at 3 atm. and falls to 1% at 175 atm.

The corresponding data for a $2CO+O_2+4N_2$ mixture (see Table V) present several features in striking contrast to the above. In the first place it will be noted that the explosion times increase progressively with pressure from 0·07 sec. at 3 atm. to 0·56 sec. at 175 atm., and all the observed maximum pressures are therefore subject to 'corrections' for heat losses during this period. Another point of interest is that the percentage carbon dioxide dissociation remains practically constant throughout at about 5·0, showing that the effect of increasing pressure is just counterbalanced by the opposite influence of increasing mean maximum temperature.

In comparing the curves in Fig. 5 attention was drawn to the fact that whereas with hydrogen the pressure rose rapidly to a maximum and thereafter fell steadily as the products of combustion cooled; with carbon monoxide there was a delay at the maximum, the pressure remaining substantially constant for an appreciable time interval. A careful analysis of the cooling curve shows that immediately after the attainment of maximum pressure there is a definite and large exothermic effect which slows down the rate of cooling; the same phenomenon is noted at all pressures above 3 atm. and increases in magnitude with increasing pressure up to about 350 atm. In this connexion it is found that if at 50 atm. the nitrogen in the $2CO+O_2+4N_2$ mixture is progressively replaced by molecular equivalents of either oxygen or carbon monoxide, the explosion times gradually diminish until, when replacement is complete, their values are, for the $2CO+5O_2$ mixture 0·005 sec. and for the $6CO+O_2$ mixture 0·01 sec. At the same time CO_2 dissociation is largely suppressed and the exothermic effect on the cooling curve disappears. Comparative data for the three mixtures $2CO+O_2+4R$ (where $R = N_2$, O_2, or CO) exploded at 50 atm. are as follows:

	$2CO+O_2$ $+4N_2$	$2CO+O_2$ $+4O_2$	$2CO+O_2$ $+4CO$
Initial pressure corrected (P_{ib}), atm.	50·75	51·30	50·75
Explosion time (t_m), sec.	0·19	0·005	0·01
Max. pressure corrected (P_{mb}), atm.	395	446	435
Percentage dissociation of CO_2 at P_m	5·1	1·8	nil
Pressure fall in 1 sec. at P_m, %	22·8	43·8	43·8
T_m, ° C. abs.	2,605	2,920	2,890

These results, by themselves, are sufficient to indicate that nitrogen is not acting merely as an inert diluent in carbon monoxide-oxygen-nitrogen explosions at high pressures; evidence is available to show that in such explosions it is 'excited' or 'activated' by the radiation emitted by the burning carbon monoxide to such a degree that it will combine readily with any excess of oxygen that may be present; in suitable circumstances, indeed, yields of nitric oxide far greater than would correspond to the attainment of thermal equilibrium have been obtained in such explosions [15, 1933]. In the absence of excess oxygen over and above that required for the combustion of the carbon monoxide, the 'excited' nitrogen molecules slowly revert to the normal state, giving off heat in the process and thus causing the marked delay in the cooling of the medium after the attainment of maximum pressure to which attention has already been directed.

TABLE V

The Influence of Varying Initial Pressures upon the Explosion of a $2CO+O_2+4N_2$ Mixture

Initial pressure (P_i), atm.	3·0	10·0	25·0	50·0	100·0	125·0	150·0	175·0
P_i corrected for compressibility (P_{ib}), atm.	3·0	10·0	25·2	50·75	101·6	126·6	149·6	172·0
Explosion time (t_m), sec.	0·07	0·10	0·15	0·19	0·40	0·47	0·53	0·56
Max. pressure (P_m), atm.	21·4	75·0	193·0	409	880	1,110	1,355	1,615
P_m corrected for compressibility (P_{mb}), atm.	21·4	74·5	189·6	395	826	1,026	1,234	1,420
P_{mb} corrected for cooling (P_{mbc}), atm.	22·9	79·5	209·0	430	898	1,112	1,339	1,555
Dissociation of CO_2 at P_m, %	5·1	5·4	4·9	5·1	5·4	5·0	5·6	5·3
Pressure fall in 1 sec. after P_m, %	58·4	42·5	31·1	22·75	19·3	18·9	17·3	13·9
Max. temperature T_m,° C.abs.	2,385	2,490	2,520	2,605	2,715	2,710	2,755	2,760

Explosions at Initial Pressures between 250 and 1,000 Atm.

At such high pressures deviations from the gas laws become very considerable and the observed gauge pressures give no indication of the actual densities of the gaseous media. The relationships between the gauge pressure (P_i) and the 'corrected' pressure (P_{ib}) as found by direct compressibility measurements are as follows [8, 1933]:

Explosive medium	*Initial pressure P_i as indicated by the gauge (atm.)*					
	75	250	350	500	750	1,000
	Ascertained 'corrected' pressure (P_{ib})					
$2H_2+O_2+3·76N_2$	74·2	238	305	392	485	560
$2CO+O_2+3·76N_2$	76·2	243·5	312·5	388·5	460	520

It is thus seen that doubling the observed gauge pressure from 500 to 1,000 atm. increases the density of the hydrogen-air medium by 1·43 and the CO-air medium by 1·34 only. The effect of increasing the initial pressure of a $2H_2+O_2+3·76N_2$ mixture from 250 to 500 atm. is to increase both the explosion time and the maximum temperature. The data given below relates to explosions in a cylindrical bomb 3 in. long and 1·5 in. in diameter.

P_i, atm.	250	350	500
P_{ib}, atm.	238	305	392
t_m, sec.	0·015	0·02	0·022
P_m, atm.	2,130	2,950	4,100
P_{mb}, atm.	1,810	2,390	3,075
T_m, ° C. abs.	2,560	2,630	2,640
Pressure fall in 1 sec. after P_m, %	72·5	64	54

Up to 500 atm. the explosions, although rapid, proceed normally, and perfectly reproducible pressure-time records are obtained. At 750 atm., however, there is an abrupt change in the character of the explosion and violent detonation is set up.

With a $2CO+O_2+3·76N_2$ mixture, on the other hand, no such abnormal effect is noticed even up to 1,000 atm.; the explosion times increase with pressure, although not nearly to the same extent as at lower initial pressures, whilst the exothermic effect observed during the cooling period after t_m reaches a maximum at an initial pressure somewhere between 350 and 500 atm. and afterwards remains constant. The data relating to these experiments are summarized below:

$2CO+O_2+3{\cdot}76N_2$ *Explosions*

	Explosion chamber 3 in. × 1·5 in.			*Explosion chamber 2·5 in. × 1·5 in.*		
P_i, atm.	250	350	500	500	750	1,000
P_{ib}, atm.	243·5	312·5	388·5	388·5	460	520
t_m, sec.	0·28	0·33	0·33	0·22	0·22	0·24
P_m, atm.	2,290	3,270	4,500	4,480	5,820	7,100
P_{mb}, atm.	1,923	2,583	3,330	3,320	4,070	4,690
T_m, °C. abs.	2,650	2,760	2,860	2,850	2,950	2,995
Calculated CO_2-dissociation at T_m, %	2·4	3·6	5·0	5·0	5·5	5·5
Pressure fall in 1 sec. after P_m, %	37	35	32·5	34·5	30	30

The Explosion of Methane-air Mixtures at High Pressure.

A mixture of composition $CH_4+O_2+3{\cdot}76N_2$ cannot be exploded at atmospheric pressure, but owing to the widening of the upper limit of inflammability it will just propagate flame at about 10 atm., the explosion time in a 3-in. diameter spherical chamber being as long as 1·22 sec. [7, 1929]. With increase of initial pressure the explosion time is considerably reduced at first (vide Table VI), but beyond about 100 atm. tends to become constant at about 0·2–0·25 sec. A slight carbon deposition accompanies the explosions at 10 and 50 atm., but this is completely suppressed at initial pressures above 100 atm.

TABLE VI

Explosions of a $CH_4+O_2+3{\cdot}76N_2$ *Mixture*

Initial pressure (P_i), atm.	9·93	48·7	95·6	143·8
P_{ib}, atm.	10·0	50·0	100·0	150·0
Max. pressure (P_m), atm.	42·0	340	775	1,200
Explosion time (t_m), sec.	1·22	0·36	0·25	0·22
Pressure fall in 1 sec. after P_m, %	45·2	29·8	24·5	22·1

The effect of the widening limits of inflammability upon the explosion of methane-air mixtures is well illustrated by the data and curves in Tables VII and VIII and Figs. 6 and 7 relating to mixtures of composition intermediate between the upper and lower limits at 10·3 and 125 atm. respectively exploded in a 3-metre diameter spherical bomb [7, 1929]. Attention may be directed to the following features:

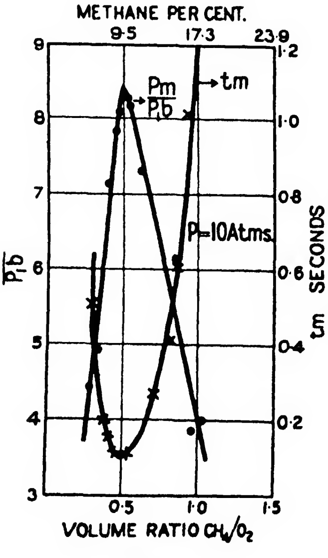


FIG. 6.

(1) The ratio of maximum to initial pressure rises sharply to a maximum corresponding, at P_i = 10·3 atm., with the theoretical mixture for complete combustion. At 125 atm. the maximum corresponds to a mixture somewhat richer in methane than the theoretical, the slight shift being probably due to some suppression of dissociation of the carbon dioxide and steam in the products.

(2) Whereas at 10·3 atm. some slight carbon deposition is observed with the upper-limit mixture, at 125 atm. it begins with mixtures far removed from the upper limit and is observed with all mixtures containing between 18·8 and 41·4% of methane. Before the upper limit is reached, however, carbon deposition ceases, and at the limit (methane = 45·5%) the products consist only of the oxides of carbon, hydrogen, formaldehyde, and steam.

TABLE VII

Data Relating to Explosions of Methane-air Mixtures

P_i = 10·3 atm. Temp. = 16° C.

	Per cent. CH_4 *in mixture*	*Volume ratio* CH_4/O_2	P_{ib} *(atm.)*	t_m *(sec.)*	P_m *(atm.)*	P_{mb} *(atm.)*	$\frac{P_m}{P_{ib}}$	$\frac{P_{mb}}{P_{ib}}$	T_m °K
Combustion complete	*6·0	0·304	10·34	0·78	44·5	43·7	4·30	4·24	1,225
	6·2	0·314	10·34	0·48	51·0	50·8	4·96	4·91	1,420
	7·7	0·397	10·34	0·15	74·0	73·4	7·15	7·10	2,050
	8·6	0·448	10·34	0·10	82·2	81·6	7·95	7·90	2,280
	9·2	0·483	10·35	0·08	84·0	83·2	8·10	8·04	2,322
	10·0	0·530	10·35	0·08	86·5	85·7	8·34	8·28	..
	10·2	0·540	10·35	0·09	85·8	85·2	8·29	8·23	..
	11·2	0·600	10·35	0·18	76·5	76·2	7·42	7·36	..
	12·8	0·700	10·36	0·27	72·5	..	7·00	..	..
	14·8	0·820	10·36	0·38	63·5	..	6·15	..	..
	†16·8	0·960	10·37	1·19	40·5	..	3·90	..	..
	*17·1	0·982	10·37	1·22	41·5	..	4·00	..	..

* Limit mixtures. † Carbon deposition began.

(3) The explosion times (t_m), which usually exceed 1 sec., reach a minimum for mixtures in the neighbourhood of the theoretical mixture for complete combustion.

(4) For mixtures containing less than the theoretical quantity of methane for complete combustion, the explosion times increase with initial pressure. Thus, for example, in the case of an 8·5% methane-air mixture at

$$P_i = 10{\cdot}3 \text{ atm.} \qquad t_m = 0{\cdot}10 \text{ sec.}$$

and at

$$P_i = 125 \text{ atm.} \qquad t_m = 0{\cdot}29 \text{ sec.}$$

With mixtures containing defect of air or oxygen the reverse is the case. Thus it is found that whilst at atmospheric pressure methane with less than two-thirds of its own volume of oxygen will not explode at high pressures, much smaller proportions of oxygen can be readily exploded. Moreover, in mixtures containing upwards of 60% of methane the effect of high pressure is not only to increase the violence of the explosion, but also to diminish, and in some cases suppress altogether, carbon deposition.

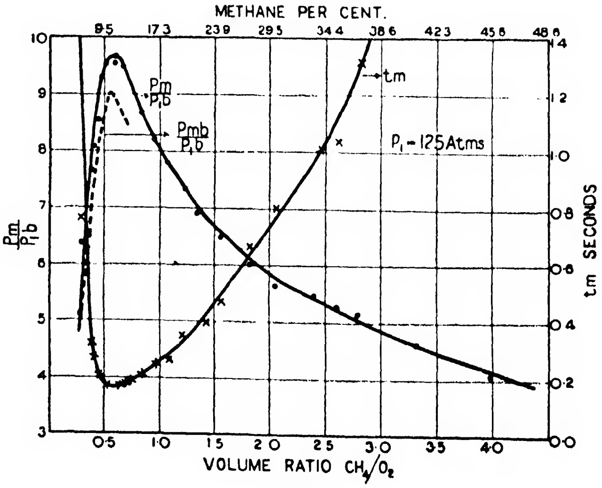


FIG. 7.

In Table IX the data for various methane-oxygen mixtures exploded at 50 atm. are compared.

TABLE VIII

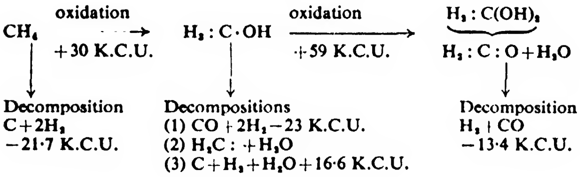
Data Relating to Explosions of Methane-air Mixtures

P_i = 125 atm. Temp. = 16° C.

	Per cent. CH_4 *in mixture*	*Volume ratio* CH_4/O_2	P_{ib} *(atm.)*	t_m *(sec.)*	P_m *(atm.)*	P_{mb} *(atm.)*	$\frac{P_m}{P_{ib}}$	$\frac{P_{mb}}{P_{ib}}$	T_m *°K*
Combustion complete	*5·7	0·288	126·2	1·58	654	588	5·18	4·66	1,345
	5·8	0·293	126·3	1·41	749	674	5·93	5·34	1,545
	6·4	0·319	126·2	0·73	821	745	6·50	5·90	1,705
	7·0	0·357	126·3	0·54	899	817	7·12	6·47	1,870
	8·0	0·415	126·5	0·38	919	885	7·66	7·00	2,021
	8·5	0·443	126·6	0·29	1,015	932	8·06	7·36	2,125
	9·4	0·494	126·8	0·17	1,121	1,027	8·84	8·10	..
	10·7	0·520	127·0	0·16	1,216	1,115	9·57	8·78	..
	11·3	0·615	127·2	0·16	1,228	1,117	9·65	8·78	..
	11·4	0·615	127·2	0·15	1,211	1,111	9·52	8·74	..
	12·6	0·680	127·4	0·15	1,198	1,105	9·41	8·67	..
	14·6	0·815	127·8	0·22	1,095	..	8·57	..	..
	16·6	0·950	128·1	0·25	1,049	..	8·19	..	..
	†18·8	1·10	128·6	0·28	1,005	..	7·82	..	..
	20·4	1·22	128·9	0·34	930	..	7·22	..	..
	22·5	1·38	129·3	0·41	893	..	6·91	..	..
	24·6	1·55	129·7	0·43	850	..	6·56	..	..
	26·3	1·70	130·1	0·41	841	..	6·46	..	..
	27·5	1·81	130·1	0·54	783	..	6·02	..	..
	31·3	2·10	131·0	0·83	744	.	5·68	..	.
	34·1	2·46	131·5	1·00	718	..	5·46	..	..
	35·6	2·63	131·9	1·03	695	..	5·27	..	..
	36·8	2·78	132·2	1·28	686	..	5·19	..	..
	38·1	3·23	132·2	1·80	675	..	5·10	..	..
	‡41·4	3·36	133·1	1·65	624	..	4·69	..	..
	*45·5	3·98	134·1	2·49	550	..	4·10	..	..

* Limit mixtures. † Carbon deposition commenced.
‡ Carbon deposition ceased.

According to the hydroxylation theory these results would be explained by the following scheme:



the intermediate products undergoing thermal decomposition or further oxidation according to circumstances. On thermodynamical grounds it seems likely that, in explosions where methane is present in considerable excess over the equimolecular proportion, any tendency there might be for some of it to decompose thermally into carbon and hydrogen would diminish with increased pressure. Also, at low initial pressures there would be a greater tendency for the oxidation to proceed as a 'non-stop' run through the monohydroxy stage to dihydroxy-methane, giving rise on decomposition to steam, carbon monoxide, and hydrogen, than for it to stop at the methyl alcohol stage.

TABLE IX

	$5CH_4+2O_2$	$2CH_4+O_2$	$4CH_4+3O_2$
P_i, atm. . . .	46·9	47·0	47·2
P_{ie}, atm. . . .	50·0	50·0	50·0
P_m, atm. . . .	381	462	635
t_m, sec. . . .	0·26	0·11	0·01
Pressure fall 1 sec. after P_m, % . . .	13·7	18·6	49·6
Composition of original medium:			
CH_4 . . .	71·0	66·3	56·6
O_2	29·0	33·7	43·4
Products:			
CO_2 . . .	3·7	3·3	6·1
CO	21·6	27·0	33·0
CH_4 . . .	22·6	12·1	3·5
H_2	52·1	57·6	57·4
Remarks:	Abundant carbon deposit		No carbon deposited

During the comparatively slow cooling of the explosion products secondary reactions occur, of which the most important are those between carbon, carbon monoxide, and steam, namely,

$$CO+OH_2 \rightleftharpoons CO_2+H_2 \pm 10{\cdot}1 \text{ K.C.U.}$$
$$C+OH_2 = CO+H_2.$$

At high pressures there will also probably be some interaction between the oxides of carbon and hydrogen resulting in the formation of methane, and steam or carbon dioxide.

REFERENCES

1. BERL, E. *Chem. and Ind.* **21**, 542, 68T (1929).
2. BERL, E., and WERNER, G. *Z. angew. Chem.* **40**, 245 (1927).
3. BONE, W. A. *Trans. Inst. Chem. Eng.* **8**, (1930).
4. —— Bakerian Lecture, *Proc. Roy. Soc., A*, **137**, 243–74 (1932).
5. BONE, W. A., NEWITT, D. M., and SMITH, C. M. *Proc. Roy. Soc., A*, **117**, 553 (1928).
6. —— —— —— *Proc. Roy. Soc., A*, **120**, 563 (1928).
7. BONE, W. A., NEWITT, D. M., and TOWNEND, D. T. A. *Gaseous Combustion at High Pressures.* Longmans, Green & Co. (1929).
8. —— —— —— *Proc. Roy. Soc., A*, **139**, 57 (1933).
9. FORT, R., and HINSHELWOOD, C. N. *Proc. Roy. Soc., A*, **127**, 218 (1930).
10. FORT R., and HINSHELWOOD, C. N. *Proc. Roy. Soc., A.*, **129**, 284 (1930).
11. NEWITT, D. M., and BLOCK, A. M. *Proc. Roy. Soc., A*, **140**, 426 (1932).
12. NEWITT, D. M., and HAFFNER, A. E. *Proc. Roy. Soc., A*, **134**, 591 (1932).
13. NEWITT, D. M., and SZEGO, P. *Chemistry and Industry*, 4 Aug. 1933.
14. —— —— *Proc. Roy. Soc., A*, **147**, 555 (1934).
15. TOWNEND, D. T. A., and OUTRIDGE, L. E. *Proc. Roy. Soc., A*, **139**, 74 (1933).
16. WIEZEVICH, P. J., and FROLICH, P. K. *Ind. Eng. Chem.* **26**, 267 (1934).

COMBUSTION RESEARCH IN COMPRESSION-IGNITION ENGINES

By G. D. BOERLAGE, *Director, Proefstation Delft*, and J. J. BROEZE, *Exp. Engineer, Proefstation Delft*
N.V. de Bataafsche Petroleum Maatschappij, Proefstation, Delft

INTRODUCTION

THE high efficiency attained in compression-ignition engines is mainly due to the utilization of an efficient air-heat cycle. The efficiency of various air cycles is dealt with in textbooks on thermodynamics; the realization of an efficient air cycle at a minimum of cost and trouble by means of the combustion of fuel oil is the main object of combustion research in C.I. engines.

The high efficiency aims at the development of maximum power for a certain engine volume or weight, or for a minimum of fuel; the low cost of residual fuels is another incentive for research.

The troubles manifesting themselves in oil engines may be due to imperfect combustion, causing smoke, smell, deposition of unburned products, and wear, which last factor involves cost of maintenance; unduly high rates of pressure-rise cause vibration of engine parts, recognizable as 'Diesel knock'.

The problems with which combustion research is concerned will be treated according to the sequence of events in the engine: I. Injection; II. Ignition; and III. The Further Stages of Combustion.

I. INJECTION RESEARCH

Injection of fuel is accomplished either by compressed air (air injection) or by directly applied pressure (mechanical or solid injection); the former method is rapidly becoming obsolete and will be considered separately.

Mechanical Injection

A. Delivery of fuel *to* spray nozzle. Aim: to feed a metered quantity of fuel at a predetermined rate.

B. Delivery of fuel *from* spray nozzle. Aim: to distribute fuel as evenly as possible through the air in the combustion space.

A. Delivery of Fuel to Spray Nozzle.

Two systems are employed:

1. *Accumulator System.* Pump supplying fuel to storage reservoir; metering of total quantity by pump, for individual cylinders by cam-controlled valve. Rate of feed controlled by fuel pressure and valve lift (McKechnie [45, 1910]).
2. *Jerk-pump System.* Pump delivering fuel directly to pulverizer, metering by variable effective stroke of pump, rate of fuel feed controlled by pump-plunger velocity. The injector may be open to the cylinder or contain an automatic discharge valve.

The pressures used for solid injection are 100–500 atm.; atomization is due to high fuel speed in the combustion space. In the jerk-pump system factors affecting metering and rate of feed are inertia and friction resistances in the pressure line, and compressibility of the oil. The resultant disturbances are pressure waves, injection lag, prolonged injection, repeated opening of fuel valve, &c., which have been dealt with, e.g. by Sass [72, 1929], Davies and Giffen [22, 1931], Berg and Rode [6, 1932], Rothrock and Marsh [69, 1934], Dicksee [24, 1935]. Compressibility of oils has been dealt with by Alexander [2, 1927], Nixon [57, 1932], Jessup [35, 1930], Le Mesurier and Stansfield [48, 1933].

Pressure-wave velocities are decreased by friction (narrow pipe, high viscosity) and are dependent on the varying bulk modulus; an average value is 4,500 ft. per sec. (1,500 metres per sec.). Viscosity affects still other parts of the delivery process, for instance the metering, which includes leakage, volumetric efficiency of pumps (Le Mesurier and Stansfield [46, 1931]), and also the correct action of valves (de Sermoise [77, 1934]). There is also the variation of viscosity with temperature (Le Mesurier and Stansfield [48, 1933]) and with pressure (Hersey [29, 1929]).

B. Delivery of Fuel from Nozzle. Spray Formation.

The introduction of the liquid fuel into the combustion chamber has two main aspects: the 'fineness' and the 'distribution' of the injected fuel in the air charge.

The 'fineness' ('micro-mixture', Boerlage and Van Dijck [15, 1934]) includes both the degree of *pulverization* and the degree of *evaporation*. The latter has often been underestimated.

The distribution refers to the degree of homogeneity of the fuel charge throughout the combustion chamber ('macro-mixture') and may be expressed in terms of fuel weight per unit of space in the chamber. Distribution includes not only *penetration* and *dispersion* by the spray proper, but also the influence of *air movement* and *air temperature*.

Both micro- and macro-mixtures change rapidly, and especially so during injection. The micro-mixture is continuously improved by progressive pulverization and evaporation, which may be counteracted to some extent by the recombining of particles, where the spray hits a surface. The macro-mixture, as primarily formed by the spray, is also continuously improved by air and gas movement; the less efficient the distribution by the spray proper, the more efficient should be the distribution by some correcting turbulence. Air injection provides a strong turbulence of its own, but for solid injection any desired turbulence must be obtained by prearranged movements of the combustion air, or, as in so-called precombustion-chamber engines and air-cell engines, by a partial combustion causing flow by means of the expanding gases.

Spray research has been concentrated mostly on the phenomenon of pulverization and on the physical factors controlling pulverization and distribution by the spray proper in still air. These matters will now be dealt with in more detail.

(*a*) **Pulverization.** (1) *General Aspect.* Bird [7, 1926] describes and Lee [40, 41, 1932–3] proves by striking photographs how pulverization results from friction of the surface of the solid jet emerging from the nozzle against the air through which the jet moves. The liquid is drawn out by the frictional forces into ligaments, which then break up and the fragments collapse into drops (Fig. 1). As long as these

At the nozzle — 1 inch from nozzle — 3 inches from nozzle

5 inches from nozzle — 7.5 inches from nozzle — 10 inches from nozzle

FIG. 1

By the courtesy of N.A.C.A.

drops have a velocity relative to the air they may be subject to further ligamentation and subsequent reduction in size. The ligament theory of pulverization implies that pulverization takes place throughout the course of the jet of oil and not at the nozzle only, as has been suggested (Triebnigg [84, 1925]). Centrifugal forces as caused by turbulent motion of the liquid through the nozzle appear to have little influence as compared with the frictional forces; only when injecting into a vacuum has the effect been remarked upon.

(2) *Influence of Physical Factors.* Internal forces in the liquid, which resist pulverization, are surface tension, as the liquid surfaces have to be disrupted and the ligaments and droplets have to be deformed, and viscosity, as deformation into ligaments and droplets requires internal flow. External forces, assisting pulverization, are air resistance and the forces created by turbulence.

Pulverization is measured by catching drops in non-solvent liquid ('Queol', Woeltjen [86, 1925]) or on sooted plates (Kuehn [39, 1925]) and counting the number of drops per gram (Bird [7, 1926]), or making individual size measurements (Haeusser and Strobl [26, 1924]); the difficulty is that pulverization is usually very uneven, whilst it is a function of jet travel as well as of jet duration. Therefore the observations of different investigators do not always tally. Moreover, evaporation should also be taken into account.

Influence of Resisting Forces. At constant viscosity increase of surface tension increases the 'break-up distance' of the jet from the nozzle (De Juhasz, Zahn, and Schweitzer [36 1932]. In practice the surface tension of petroleum fuels does not vary appreciably, even when they differ widely in viscosity, for instance. Values given (ibid.) are:

	Surface tension at 70° F. in g./sec.^2	*Viscosity const./70° F.*
Kerosine . . .	26·5	2·4 c.st.
Light Diesel oil . .	30·5	6 ,,
'Gulf heavy black' oil .	28·5	300 ,,

Viscosity has a pronounced effect on the break-up distance (ibid.), especially with plain, smooth nozzles. It was observed also that viscosity influences drop size, although no figures were given by the authors mentioned above. Tests by Kuehn [39, 1924] showing a decrease in drop size with decreased viscosity, a test by Bird [7, 1926], and indirect evidence from the penetration tests of De Juhasz and from measurements by Eichelberg [25, 1932] all point to the influence of this important fuel characteristic, and most investigators of combustion assume that increased viscosity increases the average drop size. Seeing that the viscosity of Diesel fuels may vary in a ratio from 1 to 100 at the temperatures encountered in nozzles, this field might with advantage be explored further, although the effect on the drop size is not in proportion to the great range of viscosities.

Influence of the Assisting Forces. The air resistance depends on relative oil speed and air density; increased oil speed is obtained by high injection pressure, and several investigators report on the finer pulverization so produced (Hintz [31, 1926], Sass [72, 1929], Woeltjen [86, 1925], Kuehn [39, 1925], Lee [40, 1932], Eichelberg [25, 1932]). Evidence on the influence of air density is somewhat contradictory, Sass finding a decrease in drop size with increasing air density, whereas Woeltjen and Lee report no influence.

The turbulence in the nozzle appears to have little influence when the air pressure is high, but from injection *in vacuo* it was found that turbulence causes some pulverization. Turbulence in a plain and smooth nozzle is primarily a function of oil speed in the nozzle; tests with nozzles which assist turbulent flow have been made. Lee [40, 1932] found, contrary to expectation, that pulverization from a nozzle with an insert causing swirl in the oil was less fine than without such an insert. Another matter, however, is the influence of indiscriminate turbulence. De Juhasz [36, 1932] finds the break-up distance of a jet to be a function of the Reynolds number of flow in the nozzle. Disturbances of the nozzle surface, however, may have a great effect, especially *in vacuo* (Lee). The effect of nozzle size is that in general it may be stated that smaller nozzles produce somewhat finer pulverization; the effect is small (Lee), or not felt above 0·015 in. diameter (De Juhasz), but Sass reports a great influence between 0·016 and 0·032 in. nozzles.

Though it is clear that no figure will cover actual drop sizes, the order of magnitude may be fixed practically at from 0·01 to 0·03 mm. (0·0004–0·0012 in.) (Fig. 2).

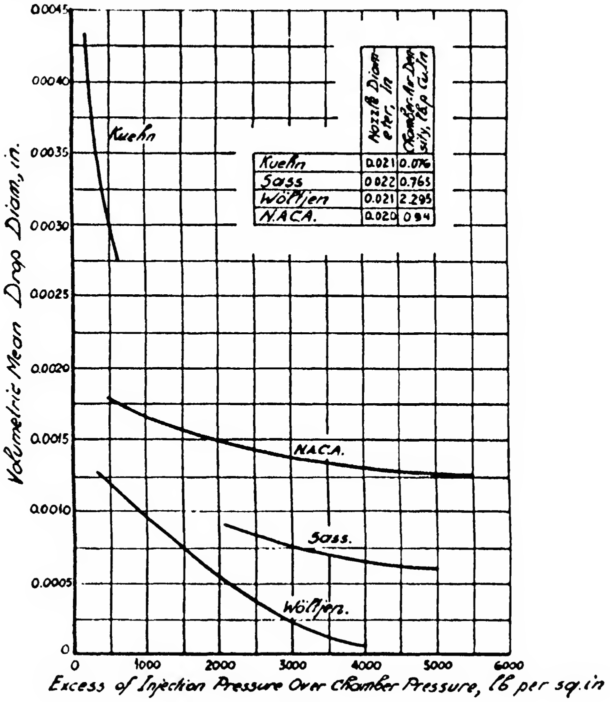


FIG. 2.

(*b*) **Distribution.** Distribution is determined by penetration and dispersion by the spray proper, and, further, mainly by air and gas movements and air temperature. Considerable data exist on this subject and prove its complexity.

(1) *Penetration.* Earlier investigators visualized penetration as the motion of the individual droplets formed at the nozzle, but Kuehn [39, 1925] pointed out that individual droplets have no penetrating power and that the distribution of a jet is due to transmission of its energy to the air, which is worked up into a flow in the direction of the spray, carrying the drops with it. As soon as some air flow exists, drops or ligaments may travel some distance before finding the greatest resistance, hence pulverization occurs all along the path of the jet (Lee [40, 1932]). This flow is thus a cause of small drops being found at even the greatest distance from the nozzle (Eichelberg [25, 1932]). Kuehn pointed out that the greater the mass of air set in motion (great dispersion) the smaller the resulting velocity of flow and,

therefore, the less the penetration. The air-flow effect has been proved by measurements of spray momentum (Riehm [65, 1924]) on continuous jets (Zahn [36, 1932]), as this was found to be sensibly constant over a large distance of penetration owing to a gradual transfer of oil momentum to the air.

Penetration has many aspects. The distance of travel of the spray tip for a certain time (tip penetration) has been studied photographically (Matthews [44, 1925], Miller and Beardsley [51, 1926], Sass [72, 1929]). Bird [7, 1926] already pointed out the importance of the penetration of the whole mass of oil, which he described as the penetration of the centre of gravity of the oil. The expression 'bulk penetration' perhaps conveys best the meaning of this characteristic, as against tip penetration. Bulk penetration has been measured by means of distribution curves obtained from oil caught during its travel by suitable catching devices (Bird [7, 1926], Schweitzer [36, 1932]). These curves show that more fuel reaches a certain plane as the distance from the jet or the air density decreases, or the oil viscosity increases, whilst the effect of increasing oil pressure may be different according to changes in the state of turbulence and pulverization caused thereby. It is possible to reduce bulk penetration by increasing the oil pressure (Schweitzer [76, 1934]), a fact well known in practice, notwithstanding the observed increase in tip penetration speed (Miller and Beardsley [51, 1926], Sass [72, 1929]). The fact that the penetration of a spray is due to the movement of the air caused by the action of the combined resistance forces of the oil particles explains that increased dispersion of a jet decreases tip-penetration speed as well as bulk penetration (Kuehn [39, 1925], De Juhasz [36, 1932]. Orifice size is a strong factor in penetration; Sass [72, 1929] found increasing tip speed with increasing nozzle size. Schweitzer found at first [36, 1932] no definite influence of orifice size on the amount of fuel that reached a certain plane; here, however, the speed of penetration has not been taken into account. Later [76, 1934] he employed another criterion, viz. the momentum of the oil spray. In contrast with the earlier momentum measurements, the test was so arranged as to allow of the measurement of the oil momentum alone. The conclusion was that the orifice size has a preponderant influence on the penetrative power, in particular at high air densities. The point is, therefore, that although spray from a small nozzle will ultimately penetrate just as far as that from a larger one, this will take a much longer time, so that for the short times available in high-speed engines the practical influence of nozzle size is very important. Whether duration of the spray has any effect on penetration has also been studied. Schweitzer has measured [76, 1934] the dynamic pressure of sprays of different duration at different distances from the nozzle. He found that for a given distance from the nozzle a dynamic pressure would only be registered from a certain injection time onwards; it then increased with further increase in injection time up to a maximum value, after which it remained constant (Fig. 3). The 'building-up' time of a spray until it reaches its maximum force increases with distance from the nozzle; it was concluded that for practical purposes injection times are always so long that the sprays may be considered fully developed over the length of travel of interest to the engine designer. This would mean that spray formation in engines can be studied on continuous sprays; some measurements (Riehm [65, 1924]) have been adversely criticized on the ground that this cannot be done. This subject is certainly of the highest importance for combustion at very high engine speeds.

(2) *Dispersion.* This subject has already been touched upon in dealing with penetration, since the two are very closely connected. The earliest measurements of dispersion have been made by spray photography (Miller and Beardsley [51, 1926], Sass [72, 1929]), taking the cone angle of the spray as a measure. As in the case of penetration, however, the external picture does not give exact information about the internal distribution. Valuable results have been obtained by actually catching the spray in containers arranged along radii in different planes perpendicular to the axis of the jet (Fig. 4) (Schweitzer [36, 1932]). The quantity of liquid passing an element of these planes can be expressed as flux and is measured as specific flux by dividing it by the space-angle formed between the nozzle and the said element.

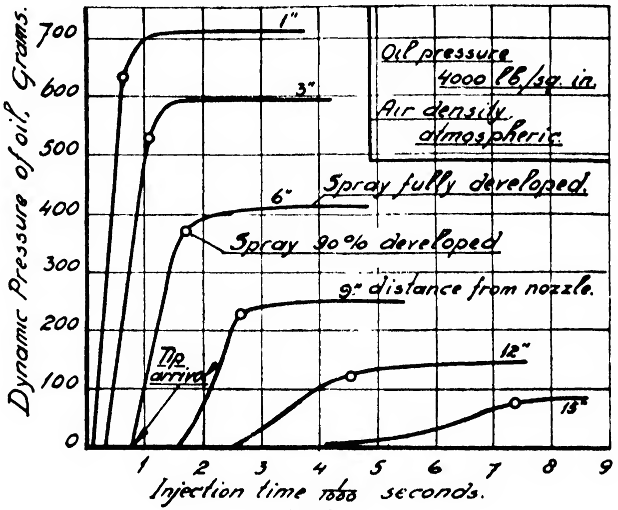


FIG. 3.

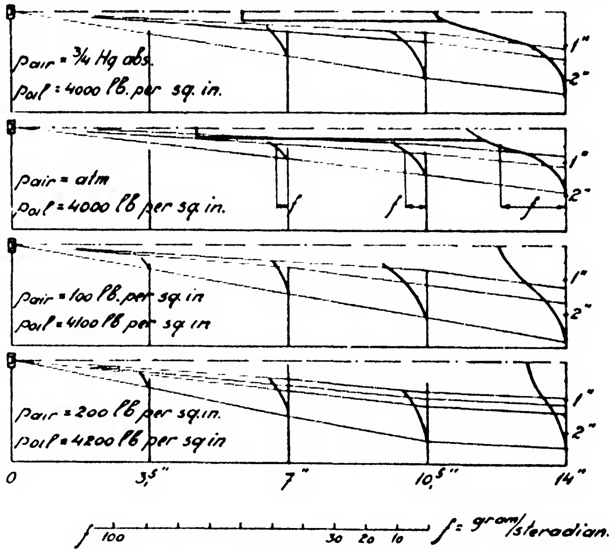


FIG. 4.

The dispersion in a given cross-section becomes more even with increasing distance, increasing air density, decreasing oil viscosity, and increasing oil pressure. This shows clearly that a compromise has to be made between dispersion and penetration.

The results of such tests as described above can give but by pressure phenomena, of which Fig. 5 gives a schematic picture on a time basis. *A* is compression, *B* expansion without fuel admission, *C*, *D*, *E*, *F* show the effect of ignition and combustion. Fuel is injected from *a* to *c*; there is first a slight fall *C* followed by a gentle rise *D*, which changes rather abruptly into the definite pressure rise *E*. Further stages of combustion *F* and expansion *G* follow. The stages *C* and *D* merge imperceptibly into each other and are generally taken together as 'ignition lag' (Hawkes [28, 1920]) or 'delay time', from *a* to *b*. The lag is mainly the time taken for preparation of the fuel for ignition, stage *C* showing that the fuel at first takes up heat from the air, and stage *D* that this is followed by a partial reaction. The end of the lag *b* represents the point where, by the heat of this reaction, a flame nucleus has been formed of such power that it ignites the rest of the fuel (Ricardo [59, 1931]).

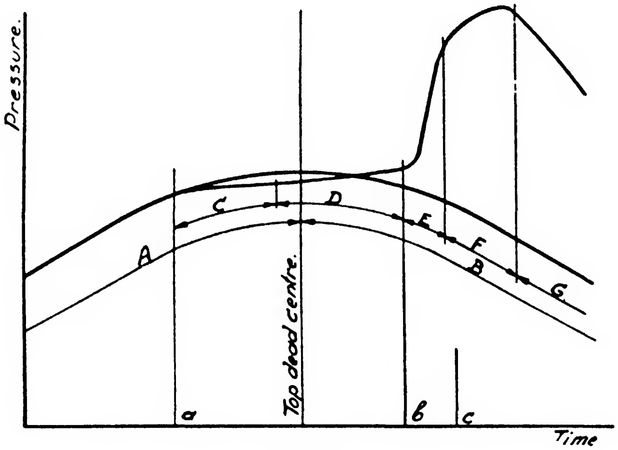


FIG. 5.

The physical and chemical aspects and the influence of physical and chemical factors will be considered hereafter.

Physical Aspect.

Opinions are divided as to the importance of evaporation of the fuel during the lag.

A. Ignition starts in Vapour Phase.

The oil drops are heated whilst travelling through the air and are gradually evaporated. The vapours thus formed are practically instantaneously heated to the temperature of the compressed air (600–900° C.) and start reaction with that air, either directly or after gasification (Rieppel [66, 1908]), or, according to more recent work, whilst decomposing (Van Dijck, Boerlage, and Broeze [12, 1932]). Heat is developed first by flameless reaction of part of the fuel, and the temperature thus rises comparatively slowly up to the point where the surplus energy liberated in some particular locality leads to a nucleus of flame (Ricardo [59, 1931]), which then spreads quickly through the mixture; in the presence of the flame the rest of the fuel is more rapidly evaporated, gasified, and burned. The ignition lag thus appears to include a period necessary for reaching an adequate (local) concentration of vapour (physical lag) and a partly overlapping period necessary for building up a flame nucleus (chemical lag) (Fig. 6). Strong evidence for this sequence of events has been given by Rothrock and Waldron's photographs of ignited sprays [67, 1934; 70, 1932], which even showed in some cases the spray to evaporate entirely before ignition, in some 1 to 2 thousandths of a sec.; in the latest, very clear, photographs by these investigators [71, 1935] the flame is shown to start from one or more tiny points, especially when the lag is relatively short (Fig. 7, *A*, *B*), proving the nuclear theory to be correct. Also after a long lag, when all the fuel is evaporated, the ignition definitely starts from a nucleus (Fig. 8, *A*).

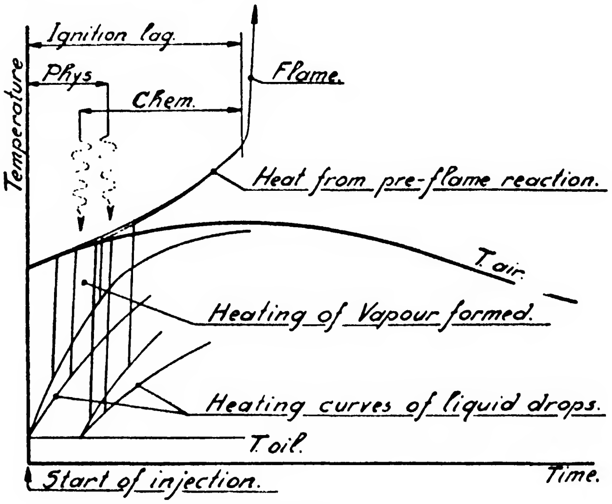


FIG. 6.

B. Ignition starts in Liquid Phase.

It has been suggested that evaporation could not be of importance (Alt [3, 1924]) as, firstly, for the usual fuels the S.I.T. (spontaneous ignition temperature) was lower than the average boiling-point. This point, however, does not hold, as the vapour pressure of a normal fuel at its S.I.T. is at least sufficient to form a combustible mixture. A second argument brought forward against evaporation was that a volatile substance like benzene was extremely difficult to ignite. Here the fact was overlooked that, although evaporation might be necessary, it might not be sufficient (benzene shows a short physical lag but a long chemical lag), vide criticism by Rothrock and Waldron [70, 1932]. It has also been suggested (Callendar [19, 1926]) that liquid drops gave a better chance for reaction because of the strained condition of the surface molecules, or because peroxides of low volatility would be formed which would recondense on the surface of any droplets [20, 1927], but Tausz and Schulte had already found [79, 1924] that oil vapours had exactly the same S.I.T. as the liquid, provided the optimal mixture strength was assured, whereas Schaefer [73, 1931] found that in the Jentzsch ignition tester, which consists of a steel crucible containing three interconnected chambers, the ignition was not initiated in the chamber in which the oil was introduced but always in one of the auxiliary chambers, which was ascribed to over-richness of the vapour mixture in the first chamber. Though in these cases it was made clear that oil may ignite as a vapour, it was contended that in the engine there was not sufficient time for evaporation; in particular, a calculation on the heating of drops during ignition lag (Neumann [54, 1927]) seemed to prove this, so that the liquid-phase theory found many supporters. These calculations, however, were based on unsatisfactory assumptions: the drop size was calculated, and was presumably 5–10 times too high; the test was made in a heated vessel, so that the assumption that

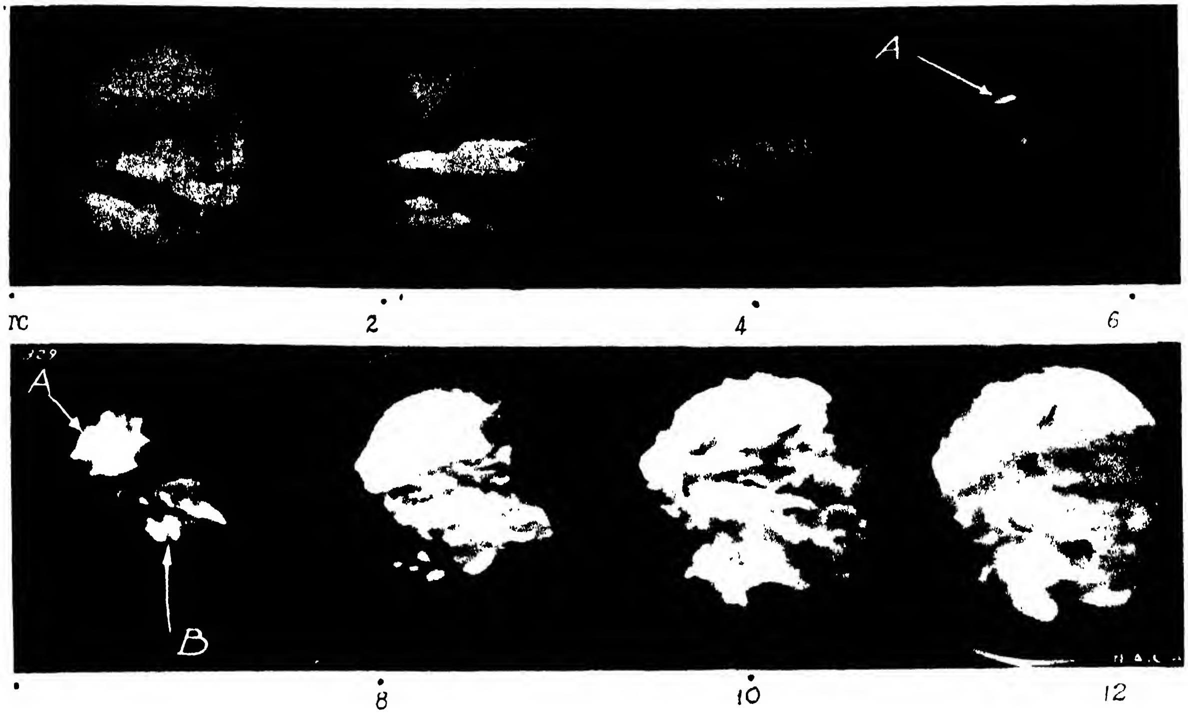


Fig. 7. Figures denote crankshaft degrees

By the courtesy of N.A.C.A.

By the courtesy of N.A.C.A.

Fig. 8. Figures denote crankshaft degrees

no fuel was heated by contact with the walls was unjustified; finally, it was assumed that the ignition lag was the time from the starting of injection up to the attainment of S.I.T. by the liquid drops, which is a debatable point. The self-ignition temperatures under pressure were determined by Tausz [79, 1924]. In later work [55, 1932] Neumann came to the conclusion that the drop surface layers entering into reaction with air must actually be evaporated during this reaction, so that ignition must indeed occur in the vapour phase.

Chemical Aspect.

Two ideas are prevalent on the chemistry of ignition, which coincide to a certain extent with the controversy about ignition in the liquid or in the vapour state. Those who visualize ignition as a drop-surface phenomenon accept the formation at low temperatures of unstable oxygen compounds (peroxide theory), whereas most of those who see ignition as a vapour reaction hold that the tendency towards decomposition of the hydrocarbon by high temperature is responsible for the reactions which lead to ignition (thermal stability theory).

A. Peroxide Theory.

Various investigators have found that on heating hydrocarbons in air at temperatures around 200° C., oxygen will be loosely bound by the hydrocarbon, forming peroxides which at higher temperatures will decompose exothermically (Tausz [79, 1924], Mardles [43, 1926]). Tausz in particular supposes a partial decomposition to take place, followed by peroxidation of the products thereof. The violent explosion of the peroxides, according to Tausz, happens at the S.I.T. and leads to instantaneous inflammation of the mixture. Others (Le Mesurier and Stansfield [47, 1932]) hold that the heat developed by the decomposition of the peroxides gradually raises the temperature of the fuel mixture and thereby the reaction velocity. This view corresponds more to the conception of the ignition nucleus.

It is interesting to note that detonation in petrol engines, another form of self-ignition, is also ascribed to the formation of peroxides, and it was shown that hydrocarbons prone to detonation readily formed peroxides, whilst substances like benzene did not (see Articles 1 and 2). The intimate relation between petrol knock and oil-engine ignition has been frequently commented upon in later years (Le Mesurier and Stansfield [46, 1931], Schweitzer [75, 1932], Boerlage and Van Dijck [15, 1934]).

Objections against the peroxide theory have been raised by Tausz himself, who found that substances which formed peroxides and which in small quantities lowered the S.I.T. of a fuel at atmospheric pressure did not do so at higher pressures. Another objection is that tetra-hydronaphthalene (tetralin), a substance which is prone to peroxidation even at normal temperature, and of which the peroxide has a strong effect in diminishing the lag of a fuel to which it is admixed, shows no strong tendency to ignite at all when used as a fuel by itself (Boerlage and Van Dijck [15, 1934]). It is suggested that fuel vapours pass so quickly through the temperature interval in which peroxides can exist that no appreciable formation takes place.

B. Thermal Decomposition Theories.

Rieppel [66, 1908] found that the coal-tar oils which gave serious ignition difficulties in Diesel engines could be distinguished from petroleum fuels by their lesser tendency to form oil gases when heated. He ascribed the tendency to ignite mainly to the quantity of hydrogen formed, and found that the hydrogen content of the fuel gave a suitable measure. This latter rule, true only for the aliphatic series and the aromatic series, has been generalized wrongly.

Criticism against the gasification theory was founded on the high S.I.T. (spontaneous ignition temperature) of fixed oil gases (Wollers and Ehmcke [87, 1921]), but it was not taken into account that at the moment when decomposition could occur in the engine the molecular fragments are not yet in equilibrium in respect of their valences (Holm [32, 1913]), so that the importance of *status nascens* had been overlooked, as well as the question of the velocity of gas formation (Magg [42, 1928]). The high S.I.T. of fixed oil gases has been used, on the contrary, as an argument in favour of the gasification theory, as it must be expected that these gases, which result from prolonged heating at high temperature, will represent (or approach to) the equilibrium state at some high temperature and will therefore be more stable when exposed again to such temperature (Boerlage and Broeze [13, 1934]). Reverting to the conception that thermal decomposition plays an important part in the ignition process, it is suggested (Boerlage, Broeze, and Van Dijck [12, 1932]) that total gasification of the fuel is unnecessary and that the reaction initiating ignition is due either to the initial stages of cracking, followed by a development of heat by the reaction of the free radicals formed with oxygen, or to oxygen reacting with the oil molecules which are in a highly strained state just prior to breaking down and so becoming abnormally sensitive to oxygen (thermal stability theory). Although, therefore, actual cracking may not take place before oxygen initiates the process, a measure for the reactivity of the fuel might then be the initial cracking velocity expressed by the number of new molecules formed per unit of time, since this corresponds to the number of fractures and therefore to the number of free valences. Determinations of this initial cracking velocity have been described [15, 1934], and it was found that a general correlation existed with the observed ignition data. Some hydrocarbons, however, gave rise to difficulties, in particular substances derived from the *iso*-butyl group, which in contrast to their low ignition quality had a high cracking velocity. This was explained later, with the aid of Rice's observation [64, 1934], that the *iso*-butyl group has not the activity usually associated with a free radical.

More recent tests, not published, by the authors, on the behaviour of hydrocarbons compressed up to 40 atm. in a motored engine in an atmosphere of nitrogen with varying percentages of oxygen, have made it clear that decomposition does not take place in any appreciable amount, unless some oxygen is present.

The Influence of Physical and Chemical Factors.

The lag being a complicated period, first of heating and evaporating fuel colder than the air, then of building up a nucleus hotter than the air in the combustion chamber, various factors exert their influence on its duration.

Physical factors are: (*a*) temperature, (*b*) pressure, (*c*) mixture conditions, (*d*) turbulence.

(*a*) **Temperature.** Air temperature is most important. The lag varies from infinity (Hawkes [28, 1920]) to less than 0·001 sec. with increasing temperature. This influence has been ascribed partly to the increased rate of heating of the droplets leading to their attaining S.I.T. earlier, but Neumann [54, 1927] in the above-mentioned calculations found the rate of heat transmission required for attaining S.I.T. so abnormally high that he concluded that it was mainly due to reaction, in particular peroxide formation, on the drop surface. In the opinion of those adhering to the theory of vapour-phase ignition it is the increased reaction velocity of the vapours at air temperature and not the rate of heating of the drops to air temperature that is responsible for the shorter lag (Boerlage and Van Dijck [15, 1934]). Fuel temperature has a far less marked effect, which proves that at least the conception of the lag as only a heating-up time is untenable. Only in the case of fuels of very high viscosity was it found that increase in temperature had a marked effect on the lag (Boerlage and Broeze [12, 1932]), this being ascribed to the improved pulverization at decreased viscosity.

Temperature of the combustion-chamber walls has a distinct effect when fuel is sprayed against the wall, as it influences the rate of evaporation, or when the turbulence system of the engine is such as to cause heat loss from or heat input into the air charge (Ricardo [60, 1931]).

(*b*) **Pressure.** Air pressure affects the lag (Bird [7, 1926]). It was found (Boerlage and Broeze [11, 1931]) in an engine that the lag was practically inversely proportionate to the compression pressure; the value of supercharging was pointed out.

A high compression ratio and low heat losses during compression are beneficial to both points (*a*) and (*b*).

(*c*) **Mixture Conditions.** These comprise a number of factors difficult to analyse. The influence of pulverization is restricted, inasmuch as there may always be a certain amount of sufficiently fine drops which will suffice by rapid evaporation to form the nucleus (Ricardo [59, 1931]), with the exception perhaps of the case just mentioned for highly viscous fuels.

It appears, however, that a certain vapour concentration will be necessary (Bird [9, 1930]) which might not always be obtained from a few drops. Bird ascribed the abnormally long lags usually found in bomb experiments to insufficient concentration and succeeded in reducing them by employing a fuel-air ratio more nearly correct. A peculiar phenomenon of ignition occurring only after several injections was also ascribed by Bird to mixture weakness; this phenomenon is well known in practice as intermittent misfiring; late ignition with a weak mixture may be found in such engines where the mixture has a chance to become homogeneous, when running at low or no load (air-injection engine).

The favourable vapour concentration must be present over a certain minimum of space to be able to develop a flame nucleus. The minute regions of varying richness around each individual droplet do not apparently count as such, since then ignition lag would be entirely independent of injection or turbulence, which, in fact, it is not; these small regions are thermally coupled with their surroundings (Boerlage and Van Dijck [15, 1934]) and cannot rise in temperature without those surroundings showing a rise too; the average vapour concentration in a space element, possibly provided with vapour from several droplets, is the determining factor.

The fact that the influence of mixture composition is only noticeable in extreme cases may be explained by the mixture being normally very heterogeneous, so that nearly always a region with most suitable conditions to start the flame will be present.

The influence of physical fuel characteristics on the mixture conditions has been treated generally under the heading 'Injection', and it will now be discussed how they affect the ignition process in practice. Viscosity has been mentioned above; the practical influence is small, since the pulverization of highly viscous fuels can be improved by adopting either preheating or high injection pressures.

Volatility will have some influence if reaction starts in the vapour phase, and if the time available to heat the drops up to the point where they can evaporate quickly enough (the physical lag) becomes of the same order as the total lag. It can be said that for normal Diesel fuels the chemical lag is usually preponderant. It has been contended that the influence of volatility is nil (Le Mesurier and Stansfield [47, 1932]), but the following table shows that in many cases the ignition lag of residual fuels is longer than that of the gas-oil fractions obtained from the respective crude oils, whereas the activity usually increases with molecular weight in the lower fractions.

TABLE I

	Cetene numbers	
Crude oil	(*a*) *Gas-oil fractions*	(*b*) *Residue*
A	60	44
B	58-60	44
C	58-60	32
D	47-49	26
E	24	39
F	30-33	24 (entire crude)
G	27	15

This table shows where, in practice, volatility may have some influence.

The longer lag of the straight-chain hydrocarbon $C_{32}H_{64}$ in comparison with lower members of the series shows that for fuels of the same chemical type some influence of volatility does indeed exist (Boerlage and Broeze [13, 1934]).

(*d*) **Air Motion.** The following general distinctions can be made between various kinds of air motion. It is often a matter of guesswork what the intensity of the different kinds of movement will be in a certain case.

(1) *Directed Air Flow* having a low velocity and a great radius of gyration, such as is caused by tangential inlet ports, screened inlet valves, or big venturi throats between cylinder and chamber. Such flow hardly disturbs the spray, it merely displaces it through the chamber after pulverization. It is unlikely that it has any effect on ignition except for such heating effect as it may have had on the air (Le Mesurier and Stansfield [47, 1932], Ricardo [60, 1931]).

(2) *Indiscriminate Turbulence* with small radii of gyration, such as is caused, e.g., by the induction turbulence of the air or by trapping part of the air during compression and forcing it into an eddying motion. The general effect of this movement is to mix the vapours with the surrounding air, which is advantageous. Neumann [54, 1927] found that in a bomb with presumably this kind of turbulence, the ignition lag at high temperatures was shorter than without this turbulence. At lower temperatures, however, the lags were longer with than without turbulence, for which no explanation was given. Two causes suggest themselves: firstly, that the fuel was mixed more homogeneously, which would have the effect of too low concentration as mentioned by Bird; secondly, that heat developed during the lag, which must cause the temperature to rise to flame temperature in some favourite nucleus, has less chance to do so when such nuclei are continuously being mingled with other parts of the charge.

(3) *Strong Air Blast*, caused when the air is forced at the end of compression through small orifices, may strongly influence the distribution of the spray, so that, apart from a beneficial effect on the evaporation of the oil and on flame propagation, too thorough mixing may occur, with its ill effects both on local fuel concentration and on the temperature rise of possible nuclei. Bird [9, 1930] and Rothrock and Waldron [70, 1932] report on such adverse influences of strong hot-air blasts on the ignition process, whilst experience in practice with engines employing such turbulence has shown similar defects, viz. a tendency to misfire at low loads and long ignition lags. The air velocities mentioned are of the order of 300-600 ft. per sec.

Chemical factors are the activity of the fuel and of the oxygen, both of which are a function of temperature.

Activity of the Fuel. The reaction velocity during the lag will be dependent on the temperature and on the concentration and activity of such part of the fuel as is liable to react most vigorously with oxygen. Activity of pure hydrocarbons in this respect, however, can best be expressed by the lag under specified conditions. Little has been published up to now about the ignition quality of pure hydrocarbons, save for some which have been proposed as standard reference fuels for calibrating the ignition lag of commercial fuels. *n*-hexadecene (cetene) was found in 1931 [11] to give a very short lag; later *n*-hexadecane has been found to give an even shorter lag (Boerlage and Broeze [13, 1934]); mesitylene, a benzene derivative (*tri*-methylbenzene) and 1-methyl-naphthalene showed such low ignition properties that they could not be used in a pure state [12, 1932]. It was suggested to use *n*-hexadecene (cetene) and 1-methyl-naphthalene as standard substances, and at the World Petroleum Congress in 1933 this was tentatively adopted [88]. In spite of the somewhat higher ignition quality of *n*-hexadecane for practical use, the use of cetene may be preferable, since cetane is only obtained via cetene and, moreover, has a somewhat higher melting-point. The cetene numbers of commercial fuels and their determination will be treated under the heading 'Light Diesel Fuels'.

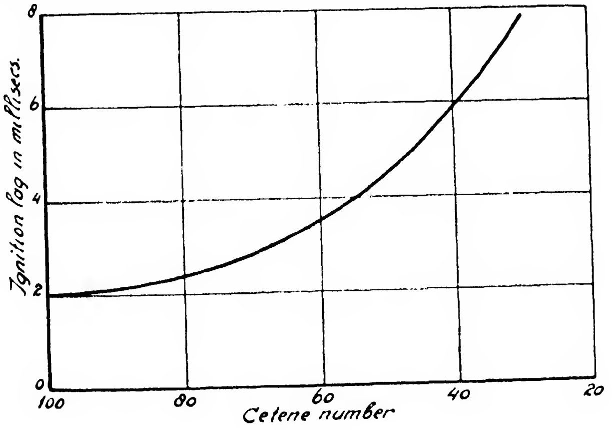


FIG. 9.

The ignition properties of 1-methyl-naphthalene are so low that under the conditions in the engines where measurements have been made it may be regarded as acting merely as a diluent. By the curve of ignition lags in a non-turbulent engine for mixtures with varying weight concentrations of cetene and 1-methyl-naphthalene it is shown that the lags are very nearly inversely proportional to the concentration of the cetene, i.e. to the concentration of the active substance in the mixture (Fig. 9).

Given pure hydrocarbons or a mixture thereof such as a petroleum fuel, the cetene value of mixtures can be calculated from the known cetene numbers of the components. The observed linear relationship between the cetene numbers (expressed in weight concentrations) is explained by the degree of activity and the concentration of the active matter (Boerlage and Broeze [12, 1932]) (Fig. 10).

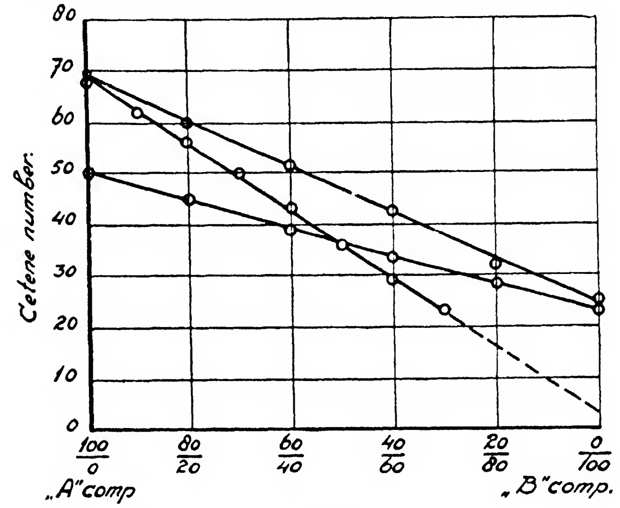


FIG. 10.

A test on an air-injection engine illustrates excellently the influence of turbulence and of the concentration of active matter in the fuel (cetene number). Fig. 11 shows the ignition lags for fuel mixtures of different cetene number and two different blast air-pressures, at constant load.

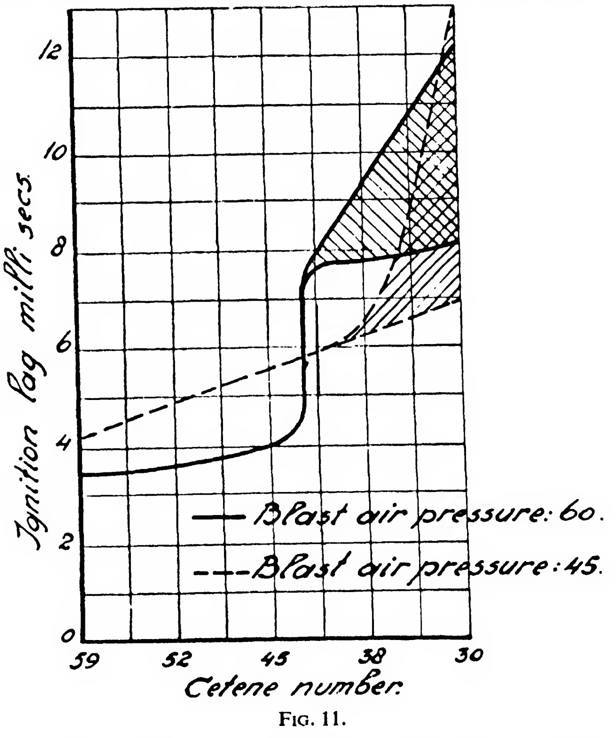


FIG. 11.

These curves have regular characteristics only over a small range in turbulent air. With high cetene numbers increased turbulence (high blast air-pressure) results in a shorter lag (proving that the cooling effect of cold blast air is of no importance), but below a certain cetene number the concentration of active matter is too low to form an early flame nucleus, and the lag undergoes an abrupt change. The lower blast air-pressure produces longer lags generally, but allows a mixture with much less active matter (lower cetene number) still to form a nucleus early. It is seen that the less the turbulence the more closely a regular shape of curve is approached.

The concentration of the oxygen is of as much importance as the concentration of active hydrocarbons. It has been found that the lag varies inversely with the oxygen concentration (Boerlage and Van Dijck [15, 1934]) and that it is actually to this that the effect of pressure mentioned has to be ascribed. This means that the effect of increased air-pressure on the transmission of heat to the fuel can be disregarded, since the presence of 4 parts of hot nitrogen to 1 part of oxygen is of no influence. This again means that the view is probably correct that heating of the fuel vapours is practically instantaneous.

The low rate of reaction during the lag makes it probable that not all the oxygen takes part in the process, but only a small part of it which is in a state of activity; this activity increases with temperature. The effect of increased temperature, however, includes also the increased activity of the fuel, so that the effect of active oxygen cannot be so studied. It is possible to introduce active oxygen into the process chemically, but such active oxygen may be entirely different from the active part of ordinary oxygen. Brooks [18, 1933] found that the addition of *ozone* to the intake air of a petrol engine had a considerable influence in promoting detonation. Tests (unpublished) have failed up to the present to produce a similar effect on ignition in a Diesel engine; it seems likely that the ozone formed unstable compounds in the petrol engine during the induction and compression strokes, whilst in the Diesel engine it may have been decomposed during the compression stroke before it had a chance to come into contact with the fuel. Ozone has been made to react with the fuel before its introduction into the Diesel engine, and for some fuels a marked increase in cetene number has resulted, although for others the influence was not noticeable (vide Table II).

TABLE II

Fuel	*Cetene numbers* (*a*) *Before*	(*b*) *After ozonizing*
A	51	70
B	49	52
C	44	70
D	44	44
E	40	46
F	40	40

This shows that certain constituents in petroleum fuels are liable to form unstable oxygen compounds at low temperatures, but the cetene numbers of the untreated fuels show that this does not always coincide with a higher ignition quality. It is therefore probable, as has been mentioned before, that firstly a tendency to form unstable oxygen compounds at low temperature plays no role in the ignition process, and secondly that the role of such compounds, if pre-formed, is merely that of introducing active oxygen which may react, after decomposition of the compound, with such active parts of the fuel as are in want of oxygen.

Another method of introducing active oxygen gives similar results, which appear to substantiate this view. The addition of a small quantity of tetralin peroxide or acetone peroxide to a fuel increases its cetene number. The curves obtained (Fig. 12) show two interesting facts: firstly, that the linear relationship of the cetene numbers with the composition of the mixtures no longer holds good; and secondly, that the effect of the admixture is generally greater according as the cetene number of the fuel to which the dope is given is higher (Boerlage and Van Dijck [15, 1934]). The inference drawn was that the more active the fuel the more useful was the active oxygen introduced, and that when a certain amount was exceeded it became gradually less useful, as in the decreased ignition-lag time there was not enough activated fuel to allow of its being utilized. It is not known at present whether the effect of other ignition-promoting dopes, such as the alkyl nitrates or nitrites (Sims [78, 1928]), can be explained in the same way.

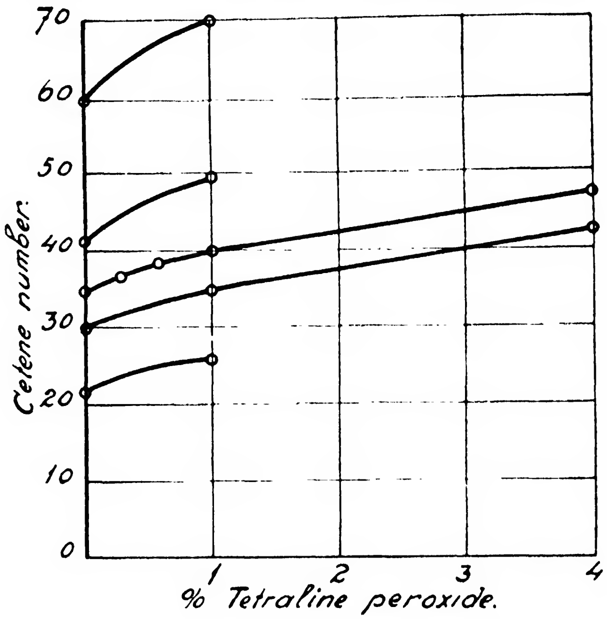


FIG. 12.

III. RESEARCHES ON THE FURTHER STAGES OF COMBUSTION

Combustion generally includes ignition, but it is practical to separate the combustion during the ignition lag, or the pre-flame combustion, from the further stages, which will be called henceforth 'combustion'. It will be considered that the ignition stage is over when the flame has been formed. Thereafter, differences in chemical structure such as influence the velocity of reaction during the ignition period appear to be no longer of importance, as the activity of the fuel under flame conditions, as far as present knowledge goes, seems to be more than sufficient, even for the present-day engines of the highest speeds, provided an adequate mixing process is available (Ricardo [60, 1931]).

We will now consider A: Analysis of combustion, and B: Influence of various factors on the velocity and completeness of combustion.

A. Analysis.

The two main lines of thought are, as for ignition: the fuel is mainly in the liquid or in the vapour phase during combustion.

Whereas Tausz [79, 1924] holds the view that the violence of the explosion of the peroxides leads to a shattering of the droplets, Wartenberg [85, 1924] visualizes the travelling droplets each leaving behind a burning vapour trail; the drops may remain in existence, gradually diminishing in weight and density, throughout their combustion (Le Mesurier and Stansfield [47, 1932]). On the other hand, those who accept considerable evaporation during ignition lag and then inflammation of the vapours, logically point to the fact that evaporation will be extremely intense in the presence of the flame (Rothrock and Waldron [70, 1932], Boerlage and Broeze [12–14, 1932–5]), and they consider that evaporation will be over before the end of combustion, unless some fuel has struck a cold wall. The main difference between the two lines of thought lies in the importance attached to the influence of more or less evaporation on spray formation.

In regard to the chemical reactions which constitute the combustion of the fuel, there are different opinions. The complicated hydrocarbon molecules may react with oxygen in two ways, viz. by hydroxylation and by destructive combustion, both of which lead to the final products CO_2 and H_2O. Hydroxylation (Bone and Wheeler [16, 1902–3]) is a sequence of reactions starting with the removal of H atoms in end positions and leading to the formation of alcohols, aldehydes, and acids of decreasing number of carbon atoms until the molecule has been consumed. Destructive combustion involves a complete decomposition of the oil molecule by the heat of the flame followed immediately by reaction of the fragments with oxygen, an old theory treated by Aufhäusser [4, 1928] and Rice [63, 1931]. Actually there may be 'a race between thermal decomposition and hydroxylation' (Haslam and Russell [27, 1926]); Sass [72, 1929] suggests partial decomposition followed by hydroxylation of the fragments. The conditions for hydroxylation are most favourable when the fuel, being well mixed, is heated gradually to flame temperature; in this case the flame is almost colourless or blue. Such combustion is found in surface-oil burners (range-burners, blue-burners for heating purposes), and in gas- and carburettor engines. The conditions for destructive burning are most favourable when the fuel is suddenly exposed to flame temperature, particularly when still unmixed with air; the yellow-white flame is caused by the presence of free carbon. The latter may also cause the flame to soot when the mixture is over-rich in hydrocarbon, or when a certain temperature is maintained, since free carbon has a definite temperature interval (about 1,200–1,500° C.) in which it is practically insensitive to the attack of oxygen (Meyer [50, 1932]). Such combustion is found in the majority of oil burners employing no other preparation of the fuel than pulverization. There is also evidence from flame photographs that the normal combustion by hydroxylation in the gas or petrol engine may turn into destructive burning, at least for part of the charge.

The fact that compression-ignition engines have a very radiant flame (Bird [7–8, 1926–7], Rothrock [70, 1932]) and a definite tendency to soot, when the mixture is locally too rich under conditions of overload or bad mixing, appears to substantiate the view that in these engines combustion is mainly of the destructive type. Hydroxylation, however, may not be entirely excluded, particularly when thorough mixing (under conditions of strong turbulence and long ignition lag) is assured.

The addition of water-vapour has served in old types of semi-Diesel engines to increase the power. The action of this water has been explained by Sass [72, 1929] as due to its effect on the dissociation equilibrium, which would lead to a more complete combustion to CO_2 than would otherwise be possible; Le Mesurier and Stansfield [46–7, 1931–2] contend that the effect of water addition is merely that of cooling the hot bulb, thereby preventing the too early ignition (pre-ignition) to which these engines with their early injection timing and unstable temperatures are prone. Whilst this is undoubtedly an important function, the point must be particularly stressed that addition of water also influences the chemical process in the direction of hydroxylation. This was found in early Russian oil-burner practice, when the beneficial effect of steam in burning mazout was discovered. It is easily demonstrated that a sooting lamp immediately becomes soot-free and less radiant when some water-vapour is introduced through the air holes of the chimney (unpublished test of H. Romp); this fact throws another light on the result obtained by Le Mesurier and Stansfield, who found [46, 1931] that addition of water materially reduced a heavy carbon formation, which was ascribed to a scouring action of the liquid water. In practice the application of water in engines is attended by many difficulties.

B. Influence of Various Factors on the Velocity and the Completeness of Combustion.

Considerations of power, fuel economy, carbon deposits, exhaust smoke, and smell all urge towards the highest possible velocity of reaction. It might be feared that a too rapid pressure rise would lead to 'knock', and vibration of structural parts of the engine, but in C.I. engines infinite reaction speed would lead to the ideal combustion diagram, Fig. 13*a*, where the rate of pressure rise is entirely under control of the engine designer, the fuel burning completely and without losses as fast as it is being injected. In reality, as is shown in Fig. 13*b*, the reaction speed is never infinite, so that combustion always lags behind the theoretical curve, producing four phases: (1) ignition lag, (2) inflammation of fuel present, (3) combustion of fuel injected farther, (4) after-burning (Fig. 13).

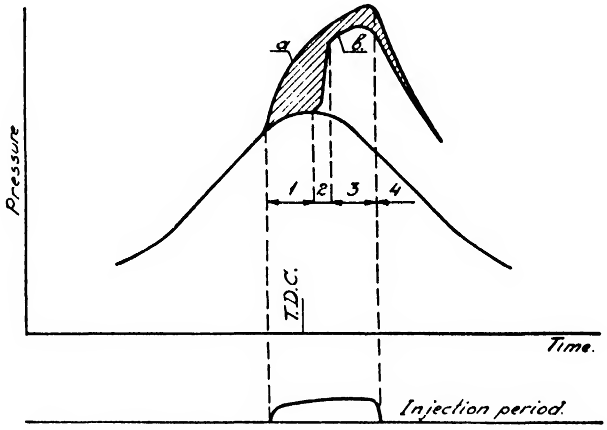


Fig. 13.

Two cases may be considered: according as the lag may be longer or shorter than the injection time.

(*a*) *The lag is longer than the injection time.* When all the fuel has been injected before the combustion sets in, the pressure rise shows an accelerating reaction velocity due to the rising temperature, up to a point where it decelerates again. The maximum rate of combustion is determined, when the mixture is perfect, by the rate of heat transmission from the flame to the unburnt mixture and the compression of that mixture by the burning gases. This is not altered by the fact that the unburnt mixture is in a condition to ignite if left by itself for some time (Sass [72, 1929]), except that it requires less external heat to bring each subsequent part up to flame temperature. It is known, further, that fuels unable to ignite by themselves can burn satisfactorily in engines when a pilot flame of self-ignitable fuel has been provided (the war-time use of coal-tar oils may be noted; vide various papers for the Diesel Engine Users Association, 1916).

In a particular and very important case the rate of heat transmission from the flame to the unburnt mixture may be too low, so that late and incomplete burning occurs, viz. in the neighbourhood of cold walls of the combustion chamber. Incomplete combustion is then caused by 'chilling' the reaction; aldehydes (Thiemann [81, 1929]) and blue vapours in the exhaust are the result. Boerlage [10, 1930] and Bouman [17, 1933] report on varnish-like deposits on cylinder walls as a result of freezing reactions. This varnish is probably a polymerization product of aldehydes and unsaturated cracked material.

When the mixture is imperfect, as is usually the case in oil engines, the rate of combustion will be further limited by the rate at which fuel will continue to find oxygen. The state of the mixture at the moment of inflammation is therefore a factor determining the maximum rate of pressure rise, which explains why the latter increases at first with the ignition lag (Le Mesurier and Stansfield [46, 1931], Boerlage and Broeze [11, 1931]) and with turbulence (Ricardo [60, 1931]). Rothrock [67, 1934] also draws attention to the fact that a very short ignition lag in his motored bomb apparatus reduced the rate of burning as well as the efficiency of combustion, which he ascribed to the imperfection of the mixture soon after the beginning of injection. Whilst his conclusion about the rate of burning can be accepted, the diminished efficiency of combustion needs some further explanation.

(*b*) *The lag is shorter than the injection time.* This is the usual case; the pressure curve is complicated by a branch (Phase 3, Fig. 13*b*, Ricardo [59, 1931]) which may closely follow part of the ideal combustion curve and is caused by fuel introduced after the flame has been formed, so that it burns rapidly as it enters the combustion chamber. After this phase, however, combustion decelerates.

We propose to call the decelerating combustion after the bulk of the fuel has been burned in both cases (*a* and *b*) 'after-burning'. After-burning is harmful because heat is developed later in the expansion stroke, and therefore less efficiently. The temperatures during the after-burning period are so high that the deceleration cannot be ascribed to insufficient activity of the fuel. After-burning becomes worse with increasing quantity of fuel injected, and is noticeable by a decreased ratio of power to quantity of fuel or to the percentage of air used (Dicksee [23, 1932]); it may be due to three causes: (1) dissociation, (2) imperfection of the mixture, (3) the above-mentioned chilling of the combustion by contact with cold walls.

(1) *Dissociation.* At high temperatures there is an equilibrium amongst the reaction products whereby they remain partly unburned until some temperature drop due to expansion has set in. It is known that for the combustion of hydrocarbons in petrol engines this dissociation is of importance (Pye [58, 1931]), but there are at present no data on this point for oil engines. Given a theoretically correct mixture, the combustion temperature in a high-compression oil engine would be higher than in a petrol engine, so that even more dissociation would be expected; on the other hand, it is not usually possible to work with fuel quantities near the correct mixture in oil engines, so that these maximum temperatures are usually lower. Dicksee [23, 1932] has suggested the possibility of dissociation accounting for after-burning in an engine with an unusually low air excess. Still, the second cause has an influence so far-reaching that in the writers' opinion Dicksee's suggestion cannot yet be unreservedly accepted.

(2) *The Imperfection of the Mixture.* This may consist either in (α) too slow evaporation of big drops (defective micro-mixture) or (β) in faulty distribution (defective macro-mixture).

(α) Too slow evaporation may be expected from fuels of low volatility (residues), which at the same time usually have a high viscosity which impairs pulverization; such fuels are liable to combustion difficulties (Bass [5, 1927]). It is known, however, that under suitable conditions heavy residual fuels will yield very nearly the same efficiency as light fuels of the gas-oil type (Hubendick [34, 1928]), which shows that too slow evaporation *per se* cannot be held responsible (Boerlage and Broeze [13, 1934]). More important is the slow evaporation resulting from over-penetration of fuel on cooled walls of the combustion chamber (Thiemann [81, 1929]). Le Mesurier and Stansfield [47, 1932] point to the coloured exhaust obtained with a fuel of low volatility, which they ascribed to over-penetration. This over-penetration is partly a distribution fault; it is extremely difficult, however, to avoid it entirely, and it is good practice to allow walls against which fuel may be sprayed to attain relatively high temperatures, such as shielded pistons (Hesselman [30, 1923]), uncooled piston crowns surrounding the entire combustion chamber (Doxford, 1916–17; Keller [37, 1928]), and heat-insulated chambers (Ricardo [61, 1931], Fig. 14). However, the heating of metal parts which are wetted by fuel may lead to carbon

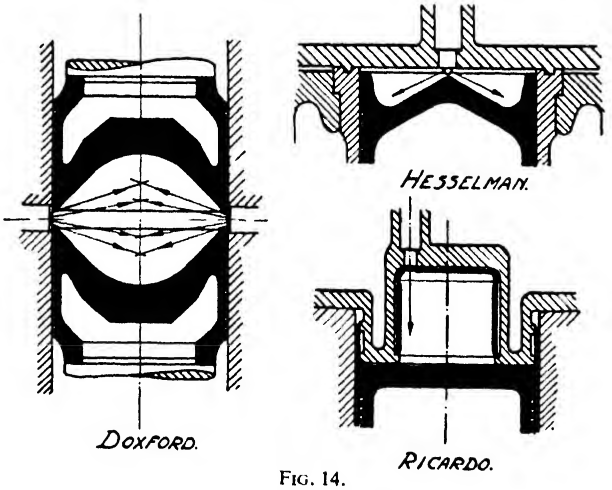


FIG. 14.

formation (Sass [72, 1929], Le Mesurier and Stansfield [47, 1932]).

The authors' opinion is that temporary deposition of fuel occurs in all oil engines to a far higher degree than is usually believed and that good scavenging will burn any carbon resulting from decomposition, whereas Sass mentions a metal temperature of 550° C. to be dangerous in respect of causing carbon. Engines with suitable turbulence may attain metal temperatures of 600° C. and higher without any carbon deposition whatever (Doxford piston, Keller [37, 1928]; Ricardo venturi plug).

The volatility of the fuel causes temporary deposition of carbon to be difficult to recognize as long as relatively light fuels are used, only slight after-burning being discernible. Besides the volatility of the fuel, the temperature of the walls and the turbulence already mentioned, the flame temperature has a profound influence on the velocity of evaporation of such deposited fuel. In a given engine at high loads this velocity of evaporation may be high, but at low loads under conditions of long ignition lag and a cold engine the burning may be slow, blue smoke being formed (Thiemann [81, 1929]), or even permanent deposition of carbon (Le Mesurier and Stansfield [49, 1934]) or of partly distilled fuel, which may give waxy or asphaltic products in chamber, cylinder oil, and exhaust manifold. Usually these deposits disappear after running on a higher load for some time.

(β) Faulty distribution may be regarded as the main stumbling-block to high combustion efficiency. Early investigators described the difficulty of finding the right compromise between dispersion and penetration of the fuel jets (Hawkes [28, 1920], low speed; Taylor [80, 1928], high speed), a difficulty which is only gradually being overcome, judging by the large amounts of excess air still quite often employed to ensure smoke-free combustion. Luckily the development of suitable supercharging apparatus has provided an easy means to obtain the filling of cylinders with large quantities of air, so that even with large excess of air a good output per cylinder is still possible, at least for the relatively slow-running class of engine. In this respect attention may be drawn to the fact that the development of high-speed supercharged engines is slow.

As long as the excess of air is big enough, the influences of various factors on the distribution is very small indeed, the fuel economy of the engine being in a large way independent of alteration of fuel quality and often even of the injection characteristics which influence spray formation. The most efficient engine under such conditions is generally that with little turbulence, implying low air resistance and low heat losses. For the utilization of larger proportions of the air leading to a high B.M.E.P. it is now generally recognized that some sort of air movement is indispensable.

The dispersion of a jet cannot apparently be increased beyond a certain amount without seriously impairing its penetration, so that unless resort is had to a large number of nozzle holes, a transverse air movement is necessary to scrub the sprays and to provide their cores with fresh air (Hesselman [30, 1923]). In large engines the number of holes may reach 10 or more, Fig. 15, but on small engines too many small orifices are impracticable, besides causing too small a penetration.

Lengthwise distribution of fuel, as has been shown, is influenced by oil pressure and viscosity and the pressure and temperature of the surrounding gases. The latter is particularly important, a fact to which attention has only recently been drawn. Two extreme cases can be considered: firstly, ignition after all the fuel has been injected, and secondly, immediate ignition. In the first case the fuel is sprayed into an atmosphere of air at, say, 600–800° C. and finds time for good bulk penetration, whilst in the latter case fuel is sprayed into flame gases of around 2,000° C., causing intensive evaporation, thereby diminishing bulk penetration. Thus, whilst the mixture at the moment of inflammation improves with the lag, as has been mentioned before, mixture throughout the further phases of combustion will be different according to the different conditions for evaporation caused by the difference in lag. Rothrock [67, 1934] warns against too short a lag, whilst Boerlage and Broeze describe a case [14, 1935] of diminished combustion efficiency caused by too short a lag, which they attribute entirely to the phenomenon described above, viz. too rapid evaporation of the fuel sprayed into the flame, which results in too little penetration. This phenomenon is of particular interest for high-speed engines, in which the ignition lag may vary with load, speed, and type of fuel used over large percentages of the injection time. Thus, apart from the optimum spray formation as given by the injection mechanism, there is an optimum ignition lag which provides the best mixture and thereby the most efficient combustion. This point has since been substantiated on different types of engine. Too rapid evaporation may also be caused by heating of the spray by hot surfaces, a fact to which Hawkes has drawn attention [28, 1920]. Apart from insufficient penetration, evaporation may also affect the 'scrubbing' by the air swirl, so that also the transverse distribution of fuel is dependent on the conditions which govern evaporation, and so on the ignition lag. The fact that low-speed engines, in which the lag is usually only a small portion of the injection time, do not seem to be affected by the above phenomena has been used as a criticism against the correctness of these views; this does not appear to be substantiated, as, firstly, with a lag that is very short the spray can probably be arranged to have a very high penetrating power, and secondly, no low-speed engines are known to the authors which give good combustion efficiency with a low excess of air. Possibly this is the very cause of the fact, which Ricardo mentions [59, 1931], that the R.A.E. research [80] led to high-speed results soon surpassing all low-speed results.

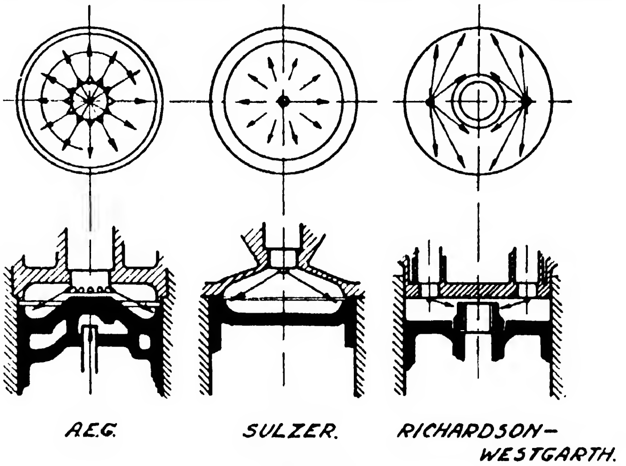


FIG. 15.

The difficulty of providing all the air with a sufficient dose of fuel without overdosing some of it, when spraying the fuel in still air, has led to the adoption of turbulence, the function of which is to intermix portions of the air charge containing under- and over-doses of fuel. The rotational swirl has been mentioned. This cannot, however, correct mixture differences of parts offset along the circular path or in the direction of the radius of swirl, as in those directions no relative motion exists. For that purpose resort is had to indiscriminate turbulence, a disorderly motion of the air superimposed on the general air motion. This turbulence is usually caused by the piston advancing toward the cylinder cover over a large part of its surface and forcing the air out from the small space left over. Some applications are shown in Fig. 14, the Ricardo sleeve-valve, and in Fig. 16, the Gardner LW. engine, both being very efficient high-speed designs employing this 'piston squish' (Alcock [1, 1934]) superimposed on rotational swirl. A recent development (Saurer, 1934) uses a piston so shaped that the 'squish' does not result in indiscriminate turbulence but in regular movement of a toroidal character. This movement is also superimposed on rotational swirl.

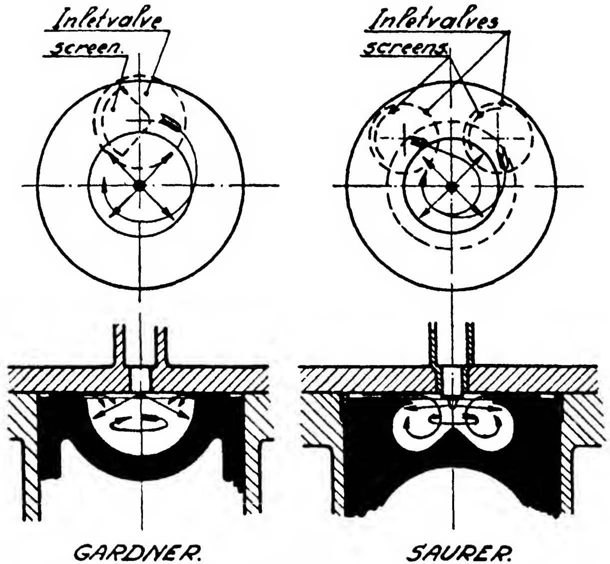


FIG. 16.

In engines employing natural air movement, the amount of movement has to be adjusted empirically to the injection characteristics to obtain optimum results (Hesselman [30, 1923], Hintz [31, 1926], Ricardo [59, 1931]).

The stronger the degree of turbulence the less the duty of the injection mechanism, so that lower injection pressures and simpler nozzles (single-hole nozzle, Ricardo [59, 1931]) may be employed. Care has to be exercised, however, in that turbulence increases heat losses (thereby possibly heat stresses), and in the case of 'induction turbulence' (i.e. the turbulence caused in the air when this is being drawn in) may lead to a diminished volumetric efficiency.

It is clear that turbulence may also correct the mixture to some extent if misadjustment of the injection mechanism occurs. A particular kind of disarrangement of the injection occurs when carbon is being formed on the injection nozzles, Fig. 17 (*a*, *b*). This occurs frequently when using unsuitable fuels containing asphalt. It results in coarse pulverization and therefore over-penetration, which again, on account of the low volatility of such fuels, leads to serious after-burning and carbon deposits throughout the combustion chamber. Intensive cooling of the nozzles (Le Mesurier and Stansfield [47, 1932]) appears to be the only effective remedy at present. It should be understood that the temperature gradient around a fuel nozzle is extremely steep and that nothing short of immediate contact of the cooling medium with the metal parts of the nozzle will ensure freedom of the trouble. This is achieved, e.g., by circulating fuel oil through a canal surrounding the nozzle piece; other constructions employing water are reproduced also in Fig. 18.

The search for greater turbulence than could be obtained by the method described above, for greater freedom in the choice of wall temperatures and for the possibility of still simpler injection systems with low injection pressures, has led to the development of engine types in which combustion takes place in an auxiliary chamber instead of in the 'open chamber' (Fig. 19*a*).

These engines are called precombustion-chamber or ante-chamber engines if only a small auxiliary chamber is provided, the function of the ante-chamber being mainly to ignite part of the fuel and gasify it, whereupon it is expelled into the main chamber by force of the pressure generated in the ante-chamber (Fig. 19*b*). There is nothing to suggest that the process of ignition in the ante-chamber is different from that in an open chamber; practical differences in the conditions are, however, firstly, that the temperature of the ante-chamber may be increased over those in an open chamber by suitable heat insulation, and secondly, that because of the small volume of the ante-chamber even at small loads all the air in it is used up, so maintaining its working temperature. The result is an ignition lag shorter than that obtainable in open-chamber engines (Le Mesurier and Stansfield [46, 1931]). At loads above that at which all the air in the chamber is used up, distribution of the remaining fuel is achieved by the turbulence created by the gases flowing out into the main chamber. Modersohn [52, 1927] found the energy available for distribution to be of the order of that of the blast air used in air-injection engines; moreover, the ante-chamber gases have a flame temperature which causes the fuel to be energetically evaporated and decomposed as well as distributed (Thiemann [81, 1929]). It has been recognized that the fuel should be injected close to the orifice between the two chambers, so that as little as possible remains in the ante-chamber after blowing-off; only rather recently has any advance been made in the shape and direction of the canals for the outflowing gases, so as to lead to higher power performance (Horiak [33, 1932]).

Engines in which the main part of the air is compressed into the auxiliary chamber are called separate-chamber engines (Fig. 19*c*). The function of this chamber is not only to provide for the ignition of the fuel but also to allow for a large proportion of that fuel to be burned therein. Greater care must therefore be taken to ensure good distribution in the chamber, which is attained in a prominent type of this class by introducing the air tangentially into the spherical chamber (Ricardo 'Comet' head, Oberhaensli, Perkins).

Insulating the metal plug in which the throat between cylinder and chamber is machined leads also to its attaining high temperatures, which increase with load and speed, so that the ignition lag expressed in angle of rotation of the crankshaft does not increase with engine speed, as it does in the open-chamber engine, but is more nearly constant (Dicksee [23, 1932]). The high temperature of the metal piece may avoid 'freezing' of the reaction of fuel sprayed against it (Ricardo [62, 1932]), thus avoiding acrid exhaust fumes and serving to evaporate fuel (Neumann [56, 1932]).

Fig. 17*a*

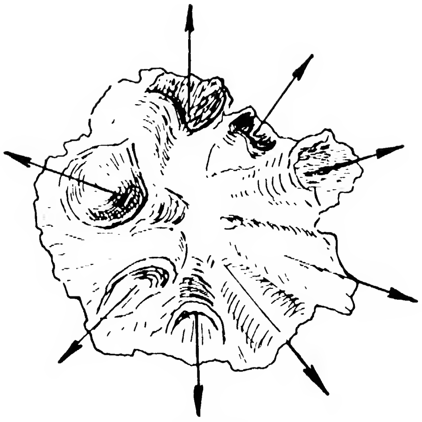


Fig. 17*b*

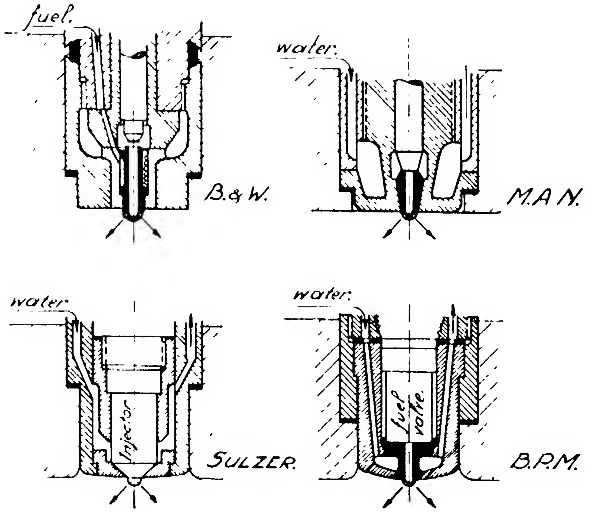
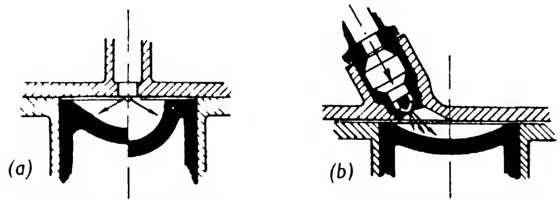
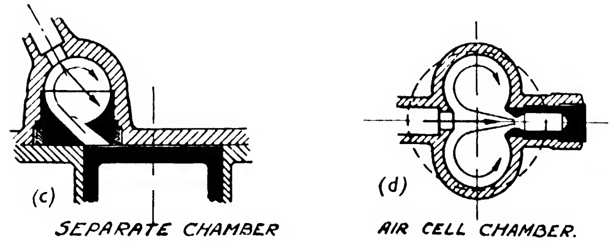


Fig. 18



OPEN CHAMBERS. ANTE CHAMBER.



SEPARATE CHAMBER AIR CELL CHAMBER.

Fig. 19

It must be recognized that in order to obtain the low air excess figures of which these engines are capable (Dicksee [23, 1932], Neumann [56, 1932]) at high loads, part of the combustion must take place in the cylinder space. The same care must therefore be taken as in the ante-chamber engine to ensure firstly, a supply of fuel to the passage leading to the cylinder, e.g. by injecting towards a point near the exit of the chamber (Ricardo [62, 1933]), and secondly, a well-directed outflow.

A third class of engine employing an auxiliary chamber is the so-called air-cell engine (Fig. 19*d*). In this type of engine, fuel is introduced in the main chamber, but part of it reaches the auxiliary chamber and burns therein, whilst the outflow of this chamber again causes a turbulence in the main chamber so as to aid distribution. A well-known example is the Lanova, Fig. 19*d*. Klaften [38, 1932] deals with the very intricate conceptions regarding the working of these types of engine. The exact mode of operation is by no means easy to understand and would carry us too far outside the scope of the present article. (*Concluded: June 1935.*)

REFERENCES

1. Alcock, J. F. Air Swirl in Oil Engines. *Engineering*, 21–8 Dec. 1934.
2. Alexander, D. H. Airless Injection and Combustion of Fuel in the High-speed Heavy-oil Engine. *Trans. I.M.E.*, Aug. 1927.
3. Alt, O. Flüssige Brennstoffe und ihre Verbrennung in der Dieselmaschine. *Dieselmaschinen*, **1**, V.D.I. Berlin, 1924.
4. Aufhäusser, D. *Brennstoff und Verbrennung*. Springer, Berlin, 1928.
5. Bass, E. L. Some Fuel Experiments in a Mechanical Injection Oil Engine. *D.E.U.A. Report*, 80, 1927.
6. Berg, S., and Rode, G. Zur Mechanik der Druckeinspritzung. *Dieselmasch.* **5**, 1932.
7. Bird, A. L. Experiments on Oil Jets and Their Ignition. *Proc I.M.E.*, Nov. 1926.
8. —— The Ignition of Oil Jets. *Proc. I.M.E.*, Dec. 1927.
9. —— Some Characteristics of Nozzles and Sprays for Oil Engines. *Trans. 2nd World Power Conference* (1930).
10. Boerlage, G. D. The Cause of Gummy Pistons. *J.I.P.T.* Oct. 1930.
11. Boerlage, G. D., and Broeze, J. J. The Ignition Quality of Fuels in C.I. Engines. *Engineering*, Nov.–Dec. 1931.
12. —— —— Ignition Quality of Diesel Fuels as expressed in Cetene Numbers. *J.S.A.E.*, July, 1932.
13. —— —— Entzündung und Verbrennung im Dieselmotor. *Forschungsheft V.D.I.* 366 (1934).
14. —— —— Combustion Efficiency in C.I. Engines. *Gas and Oil Power*, Jan. 1935.
15. Boerlage, G. D., and van Dijck, W. J. D. Causes of Detonation in Petrol and Diesel Engines. *J. Roy. Aero. Soc.*, Dec. 1934.
16. Bone, W. A., and Wheeler, R. V. The Slow Oxidation of Methane at Low Temperatures. *J.C.S.* **81** (1902), and *Proc. Chem. Soc.* **19** (1903).
17. Bouman, C. A. Lacquer Formation in Diesel and Semi-Diesel Engines. *Proc. World Petr. Cong.*, London, 1933.
18. Brooks, D. B. Ozone, Knock-inducer Extraordinary. *J.I.P.T.*, Oct. 1933.
19. Callendar, H. L. Dopes and Detonation. *Engineering*, **121**, April–May 1926.
20. —— Dopes and Detonation. *Engineering*, **123**, Feb. 1927.
21. Castleman, R. A., Jr. The Mechanism of the Atomization of Liquids. *Bureau of Standards Research Paper*, 281 (1931).
22. Davies, S. J., and Giffen, E. Injection, Ignition, and Combustion in High-speed Heavy-oil Engines. *Auto. Eng.*, June 1931.
23. Dicksee, C. B. Some Problems connected with High-speed C.I. Engine Development. *D.E.U.A. Report*, 108 (1932).
24. —— Fuel Injection. *Auto. Eng.*, March–April 1935.
25. Eichelberg, G. Heavy Oils and Their Use in Internal Combustion Engines. *Sulzer Technical Review*, no. 3 (1932).
26. Häusser, F., and Strobl, G. Die Messung der Tropfengrösse bei zerstäubten Flüssigkeiten. *Z. techn. Physik.* **5** (1924).
27. Haslam, R. T., and Russell, R. P. Fuels and their Combustion. (McGraw-Hill Book Co.), 1926.
28. Hawkes, C. J. Fuel Oil in Diesel Engines. *Engineering*, **110**, ii, 749 (1920).
29. Hersey, M. D. Viscosity of Diesel Fuel Oil under Pressure. *N.A.C.A. Techn. Notes*, 315 (1929).
30. Hesselman, K. J. E. The Hesselman Heavy Oil High-Compression Oil Engine. *Z.V.D.I.*, July 1923.
31. Hintz, H. Dieselmotoren mit Strahlzerstäubung. *Dieselmasch.* **2** (1926).
32. Holm, H. Über Entzündungstemperaturen, besonders von Brennstoffen. *Z. angew. Chem.* **26** (1913).
33. Horiak, E. Entwicklungsarbeiten an schnellaufenden Fahrzeugdieselmotoren. *Autom. Techn. Z.* **23**, Dec. 1932.
34. Hubendick, E. The Use of Heavy Oils in Internal Combustion Engines. *Trans. World Power Conference* (1928).
35. Jessup, R. S. Compressibility and thermal expansion of petroleum fuels. *Bureau of Standards Journal of Research*, Nov. 1930.
36. De Juhasz, K. J., Zahn, O. F., Jr., and Schweitzer, P. H. On the Formation and Dispersion of Oil Sprays. *Pennsylvania State College Bull.* **40** (1932).
37. Keller, K. O. Combustion and its Difficulties in Marine Oil Engines. *North-East Coast Inst. of Shipb. and Engineers* (1928).
38. Klaften, B. *Die Luftspeicher-Dieselmaschine*. Heymann, Berlin, 1932.
39. Kuehn, R. Atomization of Liquid Fuels. *N.A.C.A. Techn. Memo.* 329–31 (1925).
40. Lee, D. W. Fuel Spray Formation. *Penn. St. Coll. Techn. Bull.* **16** (1932).
41. Lee, D. W., and Spencer, R. C. Photomicrographic Study of Fuel Sprays. *N.A.C.A. Techn. Rep.* 454 (1933).
42. Magg, J. *Dieselmaschinen*. V.D.I. Berlin, 1928.
43. Mardles, E. W. J., and Stern, W. J. Dopes and Detonation. *Rep. and Memo. of the Aeron. Res. Comm.* 1062, Dec. 1926.
44. Matthews, R. Atomization obtained in Fuel Nozzles of Solid Injection Oil Engines. *Power*, no. 62 (1925).
45. McKechnie, J. B.P. 27,579 (1910).
46. Le Mesurier, L. J., and Stansfield, R. Fuel Testing in Slow and High-speed Diesel Engines. *J.I.P.T.*, 1931.
47. —— —— Combustion in Heavy Oil Engines. *North-East Coast Inst.* (1932).
48. —— —— Fuel Characteristics in Relation to Pump and Sprayer Action. *D.E.U.A. Rep.* 114 (1933).
49. —— —— Some Observations on Fuel for Heavy Oil Engines. *Inst. Marine Engineers* (1934).
50. Meyer, L. Der Mechanismus der Primärreaction zwischen Sauerstoff und Graphit (Kinetic der Kohleverbrennung). *Z. f. Physik. Chemie, Abt. B*, **17**, April 1932.
51. Miller, H. E., and Beardsley, E. G. Spray Penetration with a Simple Fuel Nozzle. *N.A.C.A. Techn. Rep.* 222 (1926).
52. Modersohn, F. Druckeinspritzung oder Vorkammerverfahren? *Dieselmasch.* **3** (1927).
53. Moureu, C., Dufraisse, C., and Chaux, R. Le Phénomène du choc et le mode d'action des antidétonants. *Ann. Comb. Liq.* **2**, 233 (1927).
54. Neumann, K. Untersuchungen über die Selbstzündung flüssiger Brennstoffe. *Dieselmasch.* **3** (1927).
55. —— Der Zündvorgang in der Dieselmaschine. *Z.V.D.I.*, Aug. 1932.
56. —— Der Oberhänsli Rohölmotor. *Dieselmasch.* **5** (1932).
57. Nixon, S. W. The Jerk-pump Injection System for C.I. Engines. *Auto. Eng.*, Jan. 1932.
58. Pye, D. R. *The Internal Combustion Engine*. Clarendon Press, Oxford, 1931.
59. Ricardo, H. R. *The High-speed Internal Combustion Engine*. Blackie & Sons, London, 1931.
60. —— *Diesel Engines*. Howard Lectures, R. Soc. of Arts, 1931.
61. —— B.P. 357,586 (1931).
62. —— B.P. 384,340 (1932) and 389,862 (1933).
63. Rice, F. O. Thermal Decomposition of Hydrocarbons. *J.A.C.S.* **53** (1931) and **55** (1933).
64. —— Thermal Decomposition of Hydrocarbons and Engine Detonation. *Ind. Eng. Chem.*, March 1934.
65. Riehm, W. Untersuchungen über den Einspritzvorgang bei Dieselmaschinen. *Z.V.D.I.*, June 1924.
66. Rieppel, P. Versuche über die Verwendung von Teerölen zum Betrieb des Dieselmotors. *Forschungsarb. V.D.I.* **55** (1908).
67. Rothrock, A. M. Photographic Study of Combustion in C.I. Engines. *J.S.A.E.*, June 1934.
68. Rothrock, A. M., and Beardsley, E. G. Some Effects of Air Flow on the Penetration and Distribution of Oil Sprays. *N.A.C.A. Techn. Notes*, 329 (1929).

69. Rothrock, A. M., and Marsh, E. T. Effect of Viscosity on Fuel Leakage, &c. *N.A.C.A. Techn. Rep.* 477 (1934).
70. Rothrock, A. M., and Waldron, C. D. Fuel Vaporization and its Effect on Combustion in a High-Speed C.I. Engine. *N.A.C.A. Techn. Rep.* 435 (1932).
71. —— —— Some Effects of Injection Advance Angle, &c., on Combustion in a C.I. Engine. *N.A.C.A. Techn. Rep.* 525 (1935).
72. Sass, F. *Kompressorlose Dieselmaschinen.* Springer, Berlin, 1929.
73. Schaefer. *Neuere Anschauungen über motorische Entzündungs- und Verbrennungsvorgänge.* Werft, Reederei, Hafen, Dec. 1931.
74. Scheubel, F. N. Zerstäubung im Vergaser. *Jahrb. d. wiss. Ges. f. Luftft.* (1927).
75. Schweitzer, P. H. Combustion Knock in Diesel Engines. *Penn. St. C. Techn. Bull.* 20 (1932).
76. —— Penetration of Oil Sprays in Dense Air. *Penn. St. C. Techn. Bull.* 40 (1934).
77. De Sermoise, C. L'Emploi de certains combustibles dans les moteurs Diesel. *La Revue des Comb. Liq.*, April 1934.
78. Sims, C. J. B.P. 294,129 (1928).
79. Tausz, J., and Schulte, F. *Über Zündpunkte und Verbrennungsvorgänge im Dieselmotor.* Knapp, Halle, 1924.
80. Taylor, H. B. High-speed C.I. Engine Research. *J. Roy. Aero. Soc.*, July 1928.
81. Thiemann, A. E. *Fahrzeug Dieselmotoren.* Schmidt & Co., Berlin, 1929.
82. —— Die Zähigkeit der Luft ist wichtiger als die Dichte für die Kraftstoffzerstäubung. *Aut. Techn. Z.* **16** (1934).
83. —— Der Einfluss der Lufttemperatur auf die Kraftstoffzerstäubung. *A.T.Z.* **6** (1935).
84. Triebnigg, H. *Der Einblase- und Einspritzvorgang bei Dieselmaschinen.* Springer, Wien, 1925.
85. Wartenberg, H. V. Verbrennungsvorgänge im Dieselmotor. *Z.V.D.I.* **68** (1924).
86. Woeltjen, A. *Über die Feinheit der Brennstoffzerstäubung in Ölmaschinen. Diss.* Darmstadt, 1925.
87. Wollers and Ehmcke. Der Vergasungsvorgang der Treibmittel im Dieselmotor. *Kruppsche Monatsh.* **2** (1921).
88. *Proc. World Petr. Cong.*, 1933. Discussion on various papers on knock rating for high-speed C.I. engine fuels.

SECTION 42

DETONATION

FOREWORD

'KNOCK' in the Internal-combustion Engine is dealt with in this series of articles. The subject has been investigated in recent years from many points of view, not only because of its importance to the fuel industry, the engine designer, and the consumer, but also because of the peculiarity of the phenomenon. Investigators who have been associated with various developments in this subject have contributed to this series. The range of articles is such that most aspects of the subject are included in it, beginning with two general articles dealing more specifically with the present views held as to the nature of 'knock' and its prevention. The subjects are then arranged according to the discussion in the leading articles, so as to treat in order and in more detail slow oxidation processes, ignition, propagation of flames, and detonation in gaseous mixtures, the study of which have led to advance of knowledge about the phenomenon. Then a series of articles describe the specific behaviour of various kinds of fuel and of 'dopes', as investigated in various countries, followed by articles discussing the methods of knock rating of fuels, and the engineering aspects of knock as affecting the spark-ignition and the compression-ignition engines.

A. C. E.

1. GENERAL STATEMENT AS TO EXISTING KNOWLEDGE ON KNOCKING AND ITS PREVENTION

By A. C. EGERTON, M.A., F.R.S.

Professor of Chemical Technology, Imperial College of Science and Technology, South Kensington

Introduction

INTERNAL combustion engines operate by the explosion of combustible mixtures which form the working fluid. The energy liberated by the combustion raises the temperature of the fluid, and pressure is exerted on the piston or moving part. In certain circumstances, depending on the fuel used, the character of the combustion changes, accompanied by a knocking sound. 'Knock' is the word which it is now the custom to use to denote this peculiar type of combustion. Sometimes 'detonation' is the expression used for the same phenomenon, but detonation usually refers to a type of combustion which is set up under rather different circumstances, so the term 'knock' is preferable.

'Knock' is mainly an engine phenomenon, though it seems possible to obtain a similar kind of combustion in a static charge in a pressure vessel [22, 1925; 38, 1928]. Its importance arises from the fact that its onset limits engine performance. Knock and pre-ignition have to be distinguished: pre-ignition, since it is an ignition which precedes the spark and occurs too early in the cycle, is often attended with thumping noise, due to excessive pressure rise before the top dead centre is reached, but it is quite different from knocking.

Not all fuels give rise to knock, and those that are prone to knock vary greatly in degree. If a petrol engine is so arranged that the compression pressure can be varied while other conditions are maintained constant, the onset of knock will occur at different values of the compression pressure for different fuels. It is possible to find in this way the highest useful compression ratio (H.U.C.R.) for a fuel; but the values so obtained depend to some extent on the design of the engine, and on the conditions of speed, load, &c., under which it is run. Some values of H.U.C.R. are given in the following table as determined by Ricardo [54, 1923] in the E. 35 variable compression engine, ignition and mixture strength being adjusted to give the highest efficiency:

Test Engine, Ricardo E. 35

Fuel	*H.U.C.R.*
Benzene . .	6·9 (pre-ignition occurs)
Cyclohexane .	5·9
Pentane . .	5·85
Hexane . .	5·2
Heptane . .	3·75
Conditions of test	1,500 r.p.m. Full throttle 30° ignition advance; 60° C. cooling water outlet.

The power output of an engine depends on the volumetric efficiency and on the compression ratio, the fuel economy mainly on the compression ratio. As the compression ratio is increased, so the efficiency increases. Theoretically (on an air-standard basis) there would be 14% gain of efficiency for an increase of the ratio from 5 to 7 : 1, and no such gain in efficiency can be obtained if, owing to the knocking characteristics of the fuel, the compression ratio cannot be raised.

An ordinary fairly heavily built engine suffers knock without much harm though the efficiency falls off as the intensity of knock increases, and eventually pre-ignition sets in owing to carbon formation, heated plugs, and other troubles, occasioned by the continuance of 'knock'. Wear may also be intensified. A high-duty engine, however, such as used for aircraft, rapidly suffers from the effect of 'knock', and gumming, pitting, and seizure soon result. Intense local attack of the metal of the cylinder head sometimes occurs. Besides the noise associated with knock, the limitation which the fuel sets upon the engine's behaviour is thus very definite, and means of eliminating knock become of great importance.

Fuels have been improved by blending of straight distillates from different localities, by the addition of cracked products or distillates from coal, or by doping with anti-knock compounds, with the result that the average compression ratio of engines has been gradually raised during the last 10 years at least half a ratio. Put in another way this means that about 2,000 million gal. per annum of petrol would otherwise have been wastefully burnt. Much depends, too, on the design of the engine cylinder head, on the position of the sparking-plugs, and on the methods adopted for advancing and retarding the ignition-spark; a suitably designed engine can work at a higher compression ratio and therefore provide a better efficiency than one using the same fuel but not designed to avoid knock. There is a limit, however, to the compression ratio which it is worth while to strive to attain for any particular type of engine. These matters are discussed in the section on 'The Engineering Aspects of Detonation' (Article 17).

Time and temperature are two important factors which influence knock. If the compressed gases are exposed to a high temperature for a long time before the flame reaches them, they will be in a condition to knock much more readily. So that the designer has to avoid a long travel for the flame, or pockets, and other conditions which can give rise to higher temperatures. Turbulence increases the rate of flame travel, and by reducing this time factor tends to allay knock. In a supercharged engine, for a given compression ratio the amount of supercharge is limited by the heat which can be removed from the cylinder to obviate such a temperature as would give rise to knock. If a better fuel is available, an increase in the amount of supercharge has more effect in increasing the power output than an increase of the compression ratio, provided the heat can be removed from the cylinder.

There will be occasion later in this article to refer to the effect of the concentration of the fuel in increasing the oxidation of a hydrocarbon, but it may be remarked here that although enrichment of the mixture may under certain circumstances give rise to knock (in accordance with the greater tendency of the fuel to oxidize), yet a rich mixture may be associated with cooler running of the engine and therefore to a decreased tendency to knock. So that there are here two effects of the enrichment which operate in an opposite manner, and it will depend on circumstances which effect predominates.

It is of obvious importance to be able to assess the knocking tendency of a fuel. But there are great difficulties. The reason for those difficulties will be obvious from what follows in this and other articles. The same fuel does not behave in the same manner in different engines in which the fuel mixture may be exposed to somewhat different conditions. Therefore, however carefully the fuel may be compared with a standard fuel in a particular engine, its comparative behaviour may be different in another engine.

It has been found that the determination in a variable compression engine of the compression ratio at which knock becomes audible (critical compression ratio) does not give very consistent results, partly because of the difficulties of measurement of the audibility and partly also because of the fact that the moment when feeble knock first occurs is sensitive to change of conditions. Co-operative efforts, therefore, have been made to standardize the methods of rating the knock tendency of fuels; a full account of these is given in this series (see Article 15 by Campbell and Boyd, and Article 16 by Stansfield). A variable compression engine (known as the C.F.R. engine from its development by the Co-operative Fuel Research Committee) has been designed specially for knock rating. The generator to which it is coupled absorbs the load and controls the speed. A bouncing-pin (cf. Article 15) acts as an indicator of the intensity of knock. When owing to the shock of the knock the pin bounces from the diaphragm on which it rests it causes an electric current to pass through a small resistance, the change of temperature of which is recorded by a thermo-couple connected to a millivoltmeter.

Fuels are matched one against another to give the same intensity of knock and are referred to a standard scale called the octane scale. This scale is based on the knock provided by a series of mixtures of 2 pure hydrocarbons, *n*-heptane which has high knocking tendency and iso-octane (2,2,4-trimethylpentane) which is a fuel which would only commence to knock at a high compression pressure, so that most fuels come within the range of the knock rating of these two pure hydrocarbons. An octane number of 70 means that the fuel when tested in the C.F.R. engine under standard conditions gives the same intensity of knock as that given by a mixture of 70 volumes of octane and 30 volumes of heptane or by a fuel which has been chosen as a subsidiary standard which gives the same knock rating as the 70% iso-octane, 30% *n*-heptane mixture. The octane number has no real significance unless the engine and conditions of the test are rigorously specified [21, 1935]. The engine conditions chosen for the test, in what is known as the 'Research Method', are speed 600 r.p.m., full load, spark advance for maximum power, mixture ratio for maximum knock, and jacket temperature 100° C., while the knock intensity is that obtained when the compression ratio is raised 1 ratio above that for the first audible detection of knock.

Owing to differences between the behaviour of different fuels and the reference fuels at different speeds, different jacket temperatures, different mixture ratios, &c., it could hardly be expected that knock ratings obtained in the above manner could tally with observations of knock which are made in many different engines in the variable conditions encountered on the road or in the air. Efforts have therefore been made to find the conditions of test which most nearly correspond to average conditions on the road. The outcome has been to develop the 'Motor Method' of test, in which the speed is raised to 900 r.p.m. and the mixture instead of being unheated has its temperature raised to 149° C. The correlation of the results obtained by this method with average results on the road is better than by the 'Research Method'; details are given in the sections concerned, in which also the many difficulties are discussed. The correlation is fairly satisfactory considering the difficulties.

One difficulty that may be referred to is that for fuels containing large proportions of olefines, aromatics, or alcohols, or for doped fuels, the comparison of knock rating with a heptane+octane mixture has to be accepted with caution, because although a mixture of naphthenic or paraffinic fuels with *n*-heptane might behave similarly to heptane+octane mixtures in such a way that 70% of the fuel of octane number 80, mixed with 30% of heptane would have an octane number 56, yet 70% of a blend with one of those other fuels might have quite another octane number; in fact, aromatic blends increase more rapidly and olefine blends less rapidly than linear relationship demands: the latter only holds approximately for blends of fuels which are mainly paraffinic (see Garner and associates [24, 1933]).

Such difficulties become more pronounced for high-rated fuels. Nowadays the tendency is to produce fuels, particularly for high-duty aircraft engines, which have octane numbers of 100 or over, and further work will need to be done before suitable methods of knock rating are developed.

With a view to this, Evans, Dodds, and Garner [21, 1935] have correlated the octane scale, with the maximum cylinder pressure in the engine, when combustion is just not such as gives rise to knock. The pressure is determined by an oscillograph indicator or by a special maximum-pressure indicator. Ordinary fuels used in engines with H.U.C.R. about 5·5 have octane numbers about 65 to 70. A difference of 10 in octane numbers between 50 and 60 corresponds to a much smaller change in compression ratio than the same difference for high octane numbers. Although the maximum cylinder pressure increases rapidly with the octane number, the change in pressure has a definite meaning, which is more than can be said of the change of octane number. The 'pick-up' unit which actuates the oscillograph so as to provide a measure of the pressure in the cylinder may indeed eventually provide satisfactory means of estimating incipient knock.

The methods of testing fuels for aircraft engines have been either similar to those adopted in the 'Motor Method' with minor modifications, or dependent on measurement of the heat developed when running on different fuels in similar circumstances in a suitable engine. (See Article 14 on 'Researches on Detonation in France', by P. Dumanois, and Article 15 on 'Measurement of Knocking Characteristics of Automotive Fuels', by Campbell and Boyd.)

Knock also has a bearing on the behaviour of the fuels used in the compression-ignition class of engine; in those engines, the fuel is injected at the end of the compression stroke into the cylinder or into the combustion chamber communicating with the cylinder. The air is heated by the nearly adiabatic compression and the injected fuel is brought to ignition by the heat received from the air or from the hot walls of the combustion chamber. There is a definite delay before the fuel ignites, occasioned to some very slight extent by the time taken for the fuel to be heated but more particularly by the time which the oxidation reactions leading to ignition take to accelerate. A short delay is an advantage provided the rate of rise of pressure is not too rapid. It is found that there is a very definite connexion between the suitability of a fuel for the compression-ignition engine and the knocking behaviour in a petrol engine. Those fuels which knock badly in a petrol engine, give short ignition delay in the C.I. engine. A straight line relationship between the cetene number of the fuel and the reciprocal of the octane number has been obtained. (See Article 14, also Article 18, by Boerlage and Broeze.) Cetene, a heavy olefine ($C_{16}H_{32}$), gives a short delay and when mixed with mesitylene (C_9H_{12}) or 1-methyl naphthalene ($C_{11}H_{10}$) or other fuel giving a long delay and therefore poor ignition characteristics, provides a reference scale against which to refer the ignition characteristics or delay of a Diesel fuel using a specified type of test engine, much in the same way as the octane scale was constructed as a reference scale for knock rating of petrol fuels.

In the combustion of a Diesel fuel when the rate of rise of pressure is high, the knocking sound is very distinct and is no doubt due to compression waves occasioned by the combustion. This will be referred to at the end of the article.

These introductory observations are perhaps sufficient to indicate the practical importance of 'knock' in its relation to engine performance, and to direct attention to the methods adopted for assessing the tendency of fuels to knock, which is obviously a matter of great importance to those industries supplying and using fuels for the internal combustion engine. Naturally the aim has been to find means of preventing knock. This has been accomplished partly by blending fuels with other products of high octane number, partly by attention to details of engine design, and also very largely by the discovery of anti-knock substances (such as 'ethyl lead'), small quantities of which when added to the fuel tend to prevent knock. It is, however, not only these practical issues that explain the lengthy, but by no means exhaustive, bibliographies of the literature of the subject which are attached to these articles, but it is the special scientific interest of the phenomenon of knock and of the behaviour of anti-knocks that is also responsible for the many investigations which have been made.

Combustion in Engines.

What happens to the combustible mixture drawn into the cylinder of a petrol engine? The mixture of fuel and air is first compressed; at a certain moment nearing completion of the compression stroke the spark passes through the mixture, and then after slight delay the flame travels through the compressed gas at a speed depending on a variety of factors: the nature of the combustible mixture, the extent of turbulence, the shape of the space in which the mixture is confined, the temperature to which the charge is brought by compression and by contact with the walls of the cylinder. The rapid bluish flame burns the mixture as it courses through it; the burning takes place in the narrow flame front, and the burnt products reach a high temperature thereby causing a very rapid rise of pressure; the energy is utilized during the expansion stroke, the pressure being exerted on the piston.

If for some reason conditions change, for instance suppose the compression pressure be increased a little, or the speed of the engine be diminished on account of increase of load, knocking may set in. As before, the flame burns the mixture at much the same speed, but at the end of the flame travel there is a sudden burst of more intense flame of whiter hue. The velocity of flame in the region where knock is initiated increases enormously (to above 300 m. per sec., though this figure is not known for certain), and the local pressure rise is very great, so great that shock waves are set up travelling back and forth through the burnt products. These compression waves give up some of their energy to the metal walls and produce sound waves in the metal which when communicated to the outside air account for the audible knock. This description of what happens is the result of visual and photographic observations [25, 1930; 37, 1927; 68, 1931; 72, 1934] (see p. 2915).

If as first discovered by Midgley [39, 1920] a small quantity of lead tetraethyl is added to the fuel, this burst of flame and the knock which accompanies it are prevented, though the velocity of the flame in the cylinder is very little changed. Nevertheless this lead compound itself readily explodes, while other anti-knocks are known, such as iron carbonyl, which are highly inflammable. What is it that causes this sudden violent type of combustion in the engine and why is it that explosive and highly inflammable substances stop, rather than enhance, the violence? These are questions which have aroused much curiosity and so account for the many investigations which have been made.

As a result of the researches of Tizard and Pye on the adiabatic ignition temperatures of hydrocarbon fuels [60, 1922; 1926] and their observations on the delay accompanying ignition, Tizard [59, 1921] had suggested in an interesting and early study of the subject that knock was mainly an effect of temperature; if the temperature coefficient of oxidation of the fuel is great enough, the higher temperature would shorten ignition delay ahead of the flame and might permit a portion of the mixture to spontaneously ignite (cf. Article 5 for further details). There was no obvious reason why very small quantities of lead tetraethyl should stop such an effect. It was also not clear whether the effect of pressure was merely a consequence of the effect of increased temperature.

During the several years following Midgley's discovery of the effect of lead tetraethyl on knock a number of investigations were made to elucidate its action and many suggestions were put forward, but it was not until about 1927 that it became clear that the processes of slow combustion which were going on in the mixture ahead of the flame were of special importance (cf. Moureu, Dufraisse, and Chaux [42, 1927], Callendar, King, and Mardles [8, 1927], Egerton and Gates [15, 1927]. From those investigations it was supposed (Egerton [13, 1928]) that knock was due to 'inequality in the condition of the charge in the engine cylinder set up in regions of high pressure and temperature, providing regions of high energy, containing molecules in high energy states where reaction can spread more quickly'. Only such hypotheses postulating centres of high reactivity in the combustible gases just prior to their ignition have survived subsequent investigations.

The difference [36, 1930] in the views of Moureu and of Callendar and their associates, on the one hand, and those of Egerton and Gates, on the other, at that time, was that the former considered that the accumulation of peroxides of the fuel was sufficient in itself to account for knock by their sudden detonation *en masse*, whereas the latter, applying to hydrocarbon combustion the theory first put forward by Semenof to account for the oxidation of phosphorus, suggested that the decomposition of the primary products of reaction caused a larger number of chains of reacting molecules to be started in a given time.

The relation of the phenomenon of knock to the chain theory of reaction is dealt with in more than one article of this series, so it is unnecessary here to elaborate what is meant by a chain reaction (see Articles 2, 3, and 4, and also the article by Newitt and Townend on 'Combustion Phenomena of Hydrocarbons' in Section 4). In this general article, it may be necessary to refer to some of the same points as are dealt with in those articles, but rather from the point of view of indicating what has yet to be learnt, than of elaborating the connexion between the chain mechanism of reactions and the phenomenon of knock.

Flame Propagation.

Before considering in more detail those combustion processes which give rise to knock, some reference must be made to the various ways in which gaseous mixtures burn. Certain sections have been included in this series which deal with flame propagation and detonation, because it is necessary to study the behaviour of flame travel in arriving at a clearer view of the nature of that type of combustion which knock constitutes (see Articles 8 and 9).

A flame is propagated very differently according to the freedom offered to the burnt products. A mixture which is ignited at the open end of a tube so that the products from the flame can expand without rise of pressure will usually propagate flame at uniform speed for some distance along the tube towards the closed end; whereas in a mixture which is ignited at a closed end so that the products cannot escape, the pressure rises and the flame accelerates. In fact, the behaviour of a flame ignited under constant volume external conditions in a closed tube is very different from that ignited under constant pressure external conditions; the nearest approach to the latter experimentally is in the soap-bubble method used by Stevens [58*a*, 1926]. The rate at which flame travels depends on a variety of factors, such as the thermal conductivity, the composition of the mixture, and the heat of the reaction; it is also influenced by the environment and by conditions which change the density of the mixture. The rate of flame travel cannot therefore be readily predicted, though some advance towards this end has been made [47, 1915; 33, 1934].

In some circumstances, a flame neither runs at constant speed nor at some continuously increasing rate, but will take a vibratory form of propagation. The amplitude may become locally very great, producing large difference of density so that the flame ceases to be propagated even after a sudden rapid enhancement of velocity. These vibratory and jerky flames, though exaggerated by the effects of resonance due to the shape of the container or tube, probably have their origin in the chemical nature of the reaction; the rate of propagation of combustion may not be an entirely uniform process, but one in which the rate may increase in certain regions amongst favoured molecules. Once irregularities arise, they quickly become enhanced due to local changes of pressure or may be to resonance effects.

In mixtures of a certain composition, containing not too much diluent gas, after a prescribed length of flame travel, the type of combustion suddenly changes; detonation occurs, and thereafter flame is propagated at a very great speed. After the first rush of flame in the region where detonation is set up, the speed settles down to a uniform rate (speeds of 1,500 metres per sec. or more). This rate can be approximately calculated on the basis of Riemann's theory of the propagation of a pressure discontinuity [11, 1899; 29, 1905–6], knowing the specific heat of the products, the energy change and the change in the number of molecules occasioned by the reaction. Flame proceeds at the same rate as the compression wave is propagated. It is possible to stop down and separate the combustion front from the compression wave [4, 1931], hindering thereby the progress of detonation; it is also possible to start the detonation wave when the compression wave is caught up by an advancing flame. Many interesting facts have been discovered about this detonating type of combustion, which have not yet been completely explained, amongst which may be mentioned the spin of the head of the detonation wave which travels in a spiral path down a tube [9, 1926; 5, 1935].

There is little doubt that compression waves set up by the flame itself bring about conditions in which detonation may occur [5, 1935]; when the flame arrives in the denser region of the crest of a compression wave, there is a great enhancement of the reaction rate and the combustion is propagated as fast as the wave, which adiabatically compresses the gas mixture as it passes through it. There is a certain limiting composition of the gaseous mixture which will no longer propagate a detonation wave [67, 1925].

Attempts have been made [16, 1927] to test the effect of temperature and pressure on the change of position for the setting up of detonation in pentane mixtures contained in a steel tube (also on the velocity of detonation of acetylene and of pentane mixtures): it was concluded from those experiments that the mixtures used in engines are probably too much diluted with nitrogen to give rise to true detonation, even under the pressure and temperature conditions in the engine cylinder. But this does not imply that some process rather similar may not occur in a small localized portion of the gas exposed to extreme conditions. There could be no propagation of a detonation wave, for the bulk of the gas would have already been burnt, but the sudden burst of reaction in the small unburnt portion which undergoes the knocking type of combustion sets up compression waves which are propagated through the products of combustion, and these can be seen in the photographic records of knocking explosions in the engine cylinder. In a true detonation—a phenomenon of great violence—the thermal energy and activity of the products of the flame and the sudden adiabatic compression, which has its origin in the sudden release of energy, provide the conditions which suddenly activate a large proportion of the molecules into reaction; whereas in the case of knock it is only in the last portion of the gas to burn, which has already been exposed to oxidation and is in an already sensitized condition, where the sudden burst of reaction occurs; no doubt the heat of the flame and the local compression contribute to the effect. Though similar perhaps in the nature of the molecular processes, which give rise to the sudden enhancement in reaction rate, detonation and knock are different as to the condition in which such enhancement is brought about. This difference is further demonstrated by the fact that anti-knocks do not delay the setting up of detonation in a tube, whereas they hinder the establishment of the knocking type of combustion [16, 1927] (cf. Article 9).

When a mixture of combustible gas is fired in a bomb under pressure, an envelope of flame travels out from the source of ignition towards the walls; the shape of this envelope is influenced by the shape of the vessel and the convection currents which are set up. As soon as the flame reaches the walls, the rate of propagation of that part which is in the vicinity of the walls is checked, and the shape of the envelope is modified. The mixture continues to burn until the flame has swept through the whole gas. In a spherical bomb the moment of maximum pressure is closely coincident with the moment when the flame reaches the walls and all the gas is burnt. This is not quite so under all

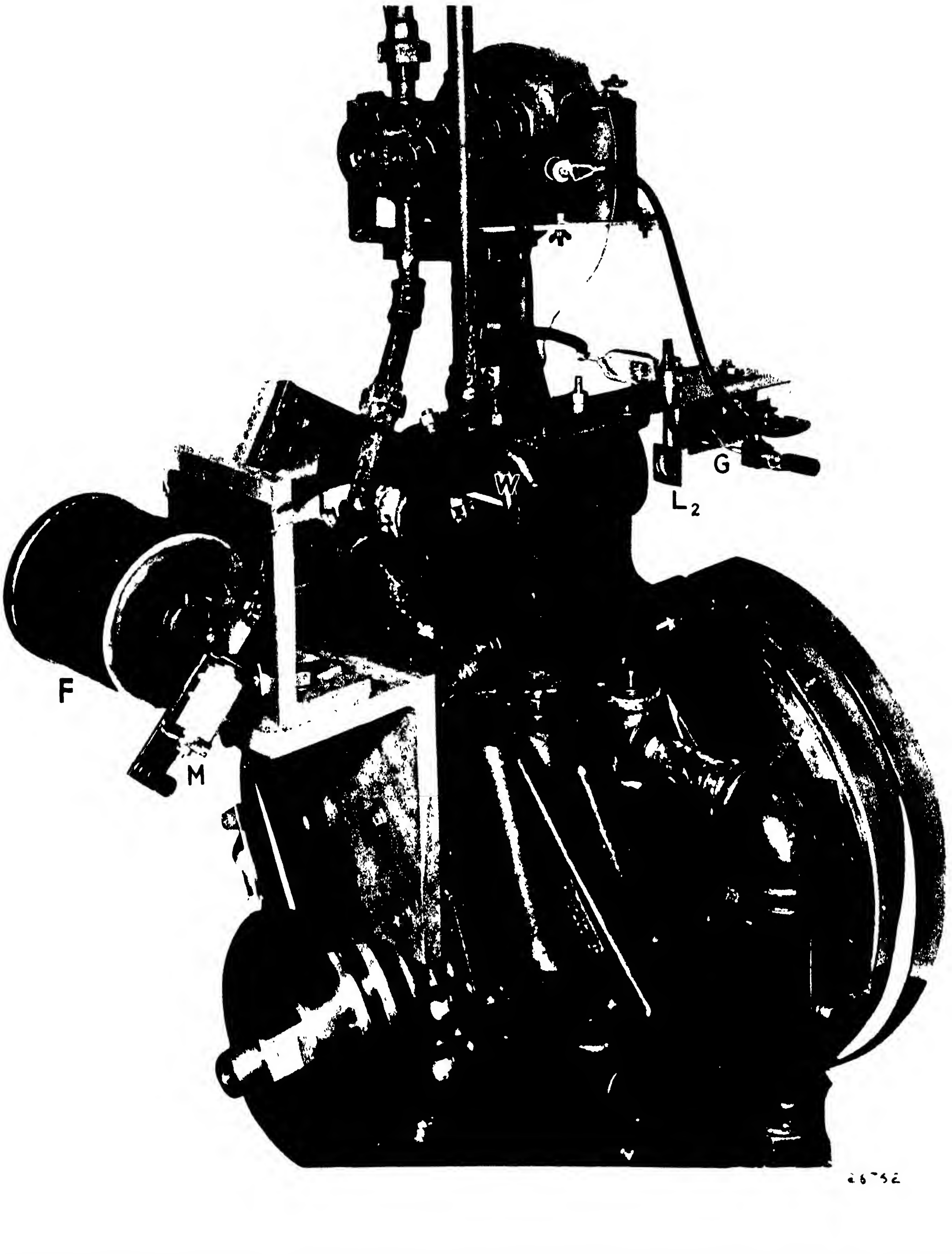


FIG. 1. Combustion Camera and Engine A. *F*, film drum case; *M*, shutter mechanism; L_1, camera lens; *W*, window; *S*, sparking-plug indicator; L_2, auxiliary lens; *G*, external spark gap

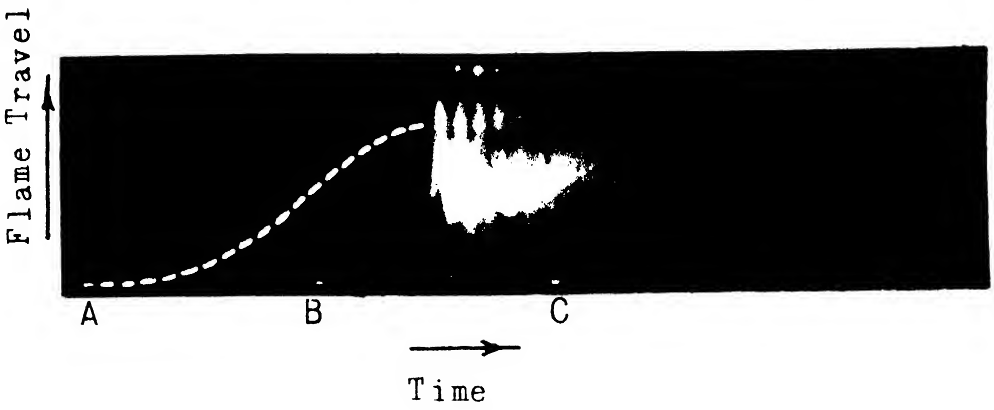


FIG. 4. Flame photograph showing pressure waves. Severe knock produced in combustion chamber B by operating the engine on normal heptane

Engine speed, 1,200 r.p.m. Spark advance, 20°. Mixture ratio, 80% theoretical air. *A*, Time of ignition. *B*, 20° after ignition. *C*, 40° after ignition

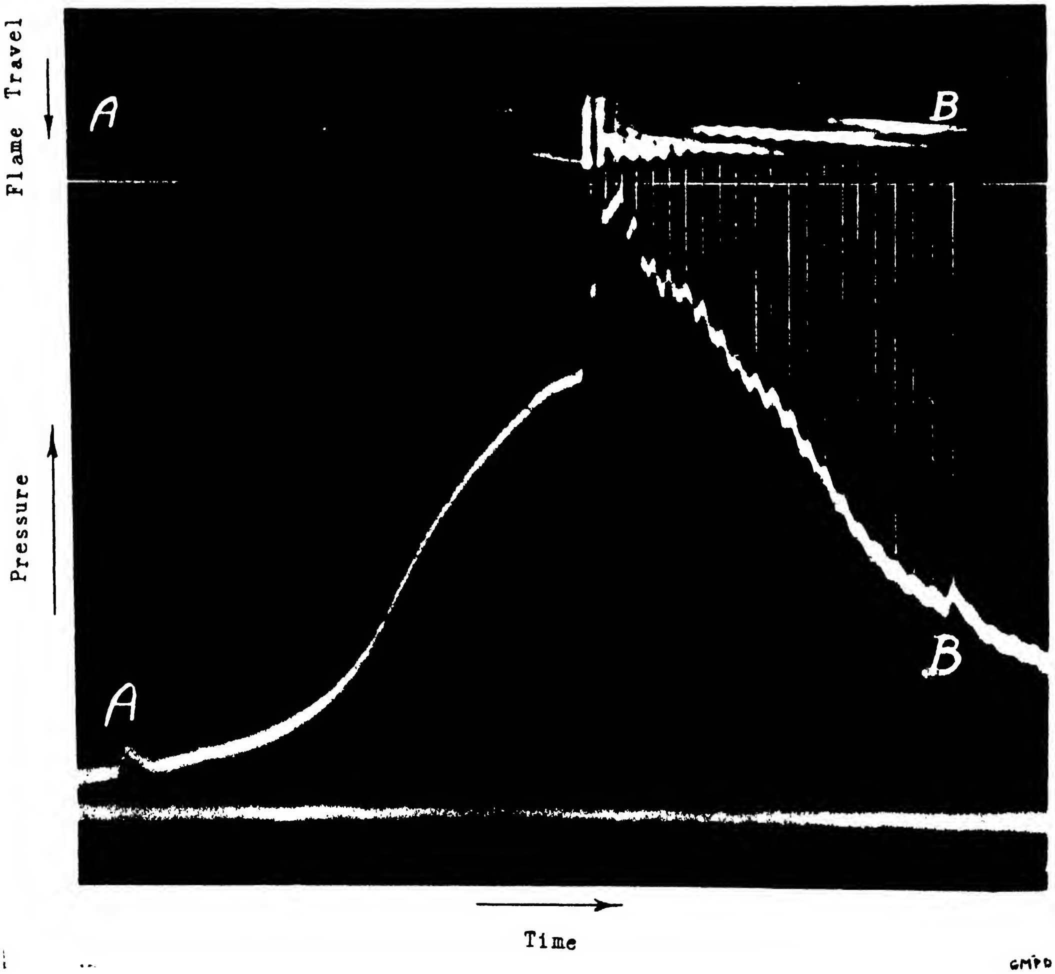


FIG. 5. The relationship between the frequencies of the shock waves on the flame photographs and the vibrations on the pressure cards at an engine speed of 100 r.p.m.

Fuel: Gasoline. Mixture ratio: 80% theoretical air. Spark advance: 40°. *A*, ignition; *B*, 91° after ignition. Full throttle circumstances, even with a spherical bomb, but in a vessel of cylindrical shape, or shape other than spherical, the moment of maximum pressure is not necessarily the moment when all the gas is burnt. In a spherical bomb just before maximum pressure is reached, the rate of pressure rise may become very great and conditions arise which lead not only to a vibratory flame but also to an explosion of the last part of the charge to burn which is very rapid and probably similar to a knocking type of explosion a more or less intense compression wave being propagated through the products of combustion [38, 1928; 41, 1935]. The rapid rate of pressure rise appears to be connected with the tendency of a fuel to knock, for those fuels which tend to knock badly give a rapid rise of pressure [10, 1929]. The rate of pressure rise depends on the reaction velocity, on the heat liberated and other factors, and a connexion with knocking tendency is not surprising (cf. Article 7 and article by Newitt and Townend, 'Combustion Phenomena of Hydrocarbons').

Successful results have attended the visual observation and the photography of flame travel in the engine, the photographic records reveal how flame travels in the cylinder; a brief description has already been given on p. 2913. The rate of flame propagation is greater than would be the case in a stationary mixture of the same composition, because turbulence assists the flame to burn the mixture by increasing the rate at which molecules are brought into the region of the flame. The shape of the combustion chamber also influences the rate of flame travel. The flame accelerates at first, and subsequently decreases or remains fairly constant, while towards the end of the flame travel a sudden very great enhancement of the rate may occur, if the knocking type of combustion sets in. Sometimes the knock seems to be set up in more than one centre, and sometimes, it occurs slightly ahead of the flame. The rate of flame travel prior to the setting up of knock is much the same whether the mixture knocks or not.

Through the courtesy of General Motors Ltd. and the publishers of *The Automobile Engineer*, photographs taken by Messrs. Withrow and Rassweiler, and by Rassweiler and Lloyd Williams of knocking explosions in an engine are here reproduced [72, 1934]. One engine (A) with which these photographic records were obtained was fitted with glass windows on both sides of the cylinder head (Figs. 1 and 2); the other engine (B) was fitted with a glass window the whole way across the upper surface of the head (Fig. 3).

The photograph (Fig. 4) gives a typical record of heavy knock using engine B: the first part of the flame-travel gives a faint record and the position of the advancing flame-edge has been marked by a heavy broken white line. The film must be understood to be travelling to the left. Where knock is set up, the record suddenly becomes very intense owing to the increase of the luminosity and the flame travels at great speed outwards from the point of knock; the pressure waves travelling back and forth are shown clearly by their effect in intensifying the luminosity of the combustion products. They are travelling at a speed of 800 or 900 metres a second.

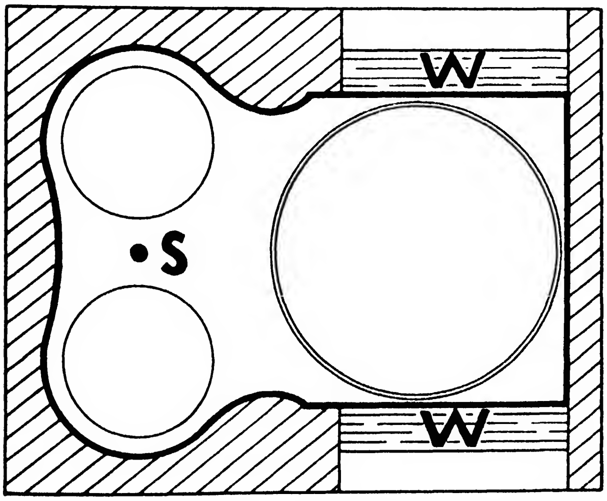


FIG. 2. Schematic diagram of combustion chamber A. S, Spark-plug location; W, Window.

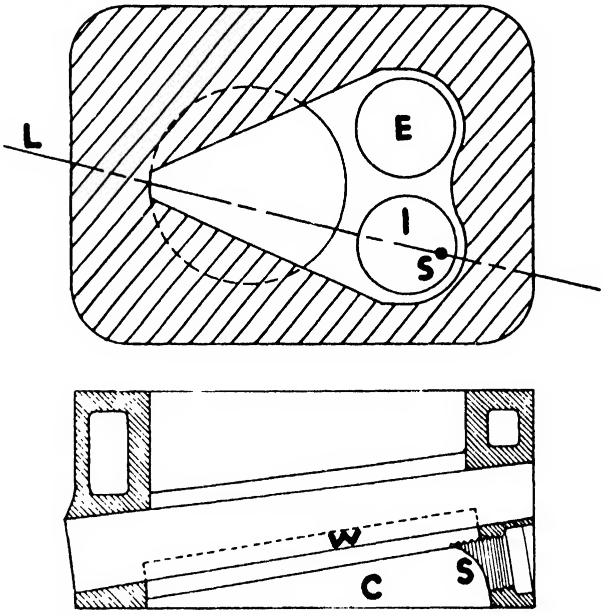


FIG. 3. Schematic diagram of combustion chamber B. S, spark-plug location; W, window; L, centre-line of window; I, intake valve; E, exhaust valve; C, combustion chamber.

Wawrzinick [73, 1932] has shown that the frequency of the vibrations set up by the combustion of gases within a bomb are also set up in the metal and are then transmitted to the external air.

There is no evidence that, prior to knock, vibratory flames make their appearance in the gases which are in a turbulent state in an engine, as they do in quiescent mixtures in bombs; the turbulence of the gases prevents such an occurrence. Similar vibrations to those obtained in the photographs of knock are seen on the pressure records (Fig. 5); as the seat of the pressure 'pick-up' unit was nearly the opposite end of the cylinder to the window, the peaks of the vibrations shown on the pressure record correspond to the minimum intensity of luminosity in the flame record. This and the following photographs were taken through the side windows using engine A.

The three flame photographs 1, 2, 3 (Fig. 6) and the corresponding pressure records show a case of violent knock (no. 1), a case of less severe knock occurring when part of the combustion had already nearly reached the wall (no. 2), and a case when a very slight knock occurred well after most of the flame had reached the walls (no. 3). The movement of the particles indicates that the backward flow of the burnt gas is of the same order as the forward movement of the flame, but when knock occurs there is a sudden movement of gas. It must be noted that the window only views the last part of the charge to burn and does not depict the whole run of the flame which has a speed of about 55 ft. per second.

The flame front may be complex and give rise to two knocks as Fig. 7 indicates. The shape of the flame and the depth of the flame along the line of sight have to be taken into account in interpreting these records. If the foremost portion of the flame front touched the end wall of the combustion chamber prior to knock, the last part of the charge to burn would be separated into two sections by a wall of flame and by the combustion-chamber walls; the record can be interpreted as the result of knock occurring in these two regions at slightly different times.

The form of the flame front at the inception of knock and the shape of the combustion chamber influence the extent of the knock which occurs. Knock may occur after peak pressure because, owing to the rounded shape of the flame, a portion of the charge may be unburnt although part of the flame may have reached the end wall. The considerable differences observed from cycle to cycle are no doubt due to the irregularity in the shape of the flame brought about by differences of turbulence and of admixture. When severe knock occurs before any of the flame reaches the cylinder wall, then there is no evidence of multiple knock.

It is noteworthy that anti-knocks such as lead tetraethyl have little effect in delaying the travel of flame of a mixture in a pressure vessel, unless the flame travel is slow and vibratory [16, 1927] and unless the anti-knock is already decomposed (and probably oxidized) prior to the arrival of the flame [34, 1931] (see Article 9, 'Ignition and Flame Movement' by G. B. Maxwell and R. V. Wheeler).

These facts indicate that the processes which occur in front of the flame during the heating of the gaseous mixture by the flame, and which tend to accelerate the reaction and give rise to knock, are hindered by the anti-knock but only when it is in the right form to be effective. The anti-knock has little effect on the normal rate of flame travel in the engine, certainly none on the setting up of true detonation in a detonating mixture and apparently very little effect on the adiabatic ignition temperature [51, 1927].

The above discussion establishes that knock is a result of intense compression waves occasioned by the enormously enhanced rate of combustion which occurs in the last part of the charge to burn when exposed to certain conditions of pressure and of temperature. If the rate of rise of pressure is great, the local concentration of reactants increases, and the loss of energy for a given volume is diminished, with a consequent rise in reaction rate. The temperature to which the gases are exposed not only influences the reaction rate but substances are evidently formed by slow oxidation prior to the actual arrival of the flame which affect the subsequent rate of combustion. To what extent such substances are produced as a result of the temperature of the flame itself or as a result of the hot surfaces to which the gases are exposed cannot yet be exactly stated; but the facts that length of flame travel, temperature of valves, carbonized surfaces all favour knock are significant in showing that it is not merely a matter of the effect of the temperature of the flame (see p. 2921).

Combustion prior to Inflammation.

This discussion leads to consideration of those processes which precede inflammation. What happens in that stage of the process of combustion corresponding to the heating from normal temperature up to such temperatures for which the reaction rate is rapid enough for inflammation to take place?

It has only been in the last 10 years that detailed studies have been made upon what really happens when a gas like hydrogen combines with another like oxygen. The result of the reaction, its dependence on temperature and many facts about the reaction (like the temperature at which ignition could be expected to occur under certain circumstances) were known well enough, but exactly how the various atoms proceeded to combine to form water under various circumstances was quite unknown and in spite of quite a vast recent literature recording extensive investigations there is yet much to learn about the process. If the kinetics of the reaction $2H_2+O_2 \rightarrow 2H_2O$ are only partially elucidated, it is still less to be expected that the mechanism of such reactions as occur in the oxidation of hydrocarbons (e.g. $C_6H_{14}+9{\cdot}5O_2 \rightarrow 6CO_2+7H_2O$) should be as yet fully understood.

Bone and his associates (cf. article by Newitt and Townend on 'Combustion Phenomena of Hydrocarbons') had investigated what was formed in the slow oxidation of such vapours as methane, ethane, ethylene, acetylene, &c., and though they proposed a mechanism known as the 'hydroxylation theory of hydrocarbon combustion' wherein the several successive oxidation products were considered as formed by the progressive hydroxylation of the hydrocarbon, the actual molecular mechanism was not precisely defined. This theory is successful in so far as it defines the nature of the products likely to be formed. The higher hydrocarbons are, however, fairly complicated molecules, so that not only the number of possible products of oxidation are large, but the number of paths along which the reaction can proceed may be numerous.

Before considering the oxidation of hydrocarbons, brief reference will be made to the simpler case of hydrogen. There are several ways in which hydrogen can be oxidized: (*a*) photochemically, (*b*) by photosensitization, with H, O, or OH atoms and radicals produced by active Hg atoms or other means, (*c*) by heterogeneous surface action, or (*d*) by homogeneous thermal reaction in the gas phase.

(*a*) Photochemical investigations have shown that the absorption of light can give rise to oxygen atoms and that these in turn set up a reaction chain in which hydrogen atoms are also produced. The U.V. light absorbed has sufficient energy to dissociate the oxygen molecule, the oxygen atoms so formed start the chain reaction:

Production of H atoms: $H_2+O \rightarrow H+OH$

$$\text{Chain}\left\{\begin{array}{l} \quad O_2+H \rightarrow HO_2 \\ \qquad\quad \uparrow \qquad \downarrow \\ H_2O_2+H \leftarrow HO_2+H_2 \end{array}\right.$$

The chief product is hydrogen peroxide; this appears to be formed mainly by the above mechanism, but many other processes [57, 1935] can occur some of which can stop the chain such as:

$$\begin{array}{l} O+O_2 \rightarrow O_3 \\ OH+OH \rightleftarrows H_2O_2 \text{ or } H_2O+O \\ HO_2+HO_2 \rightarrow H_2O_2+O_2 \\ OH+HO_2 \rightarrow H_2O+O_2. \end{array}$$

HO_2 and H are the chain carriers, being continuously reformed and bringing into reaction fresh oxygen and hydrogen molecules; this chain mechanism explains why a single quantum of light absorbed which can only produce two initial oxygen atoms, can provide a large yield of product.

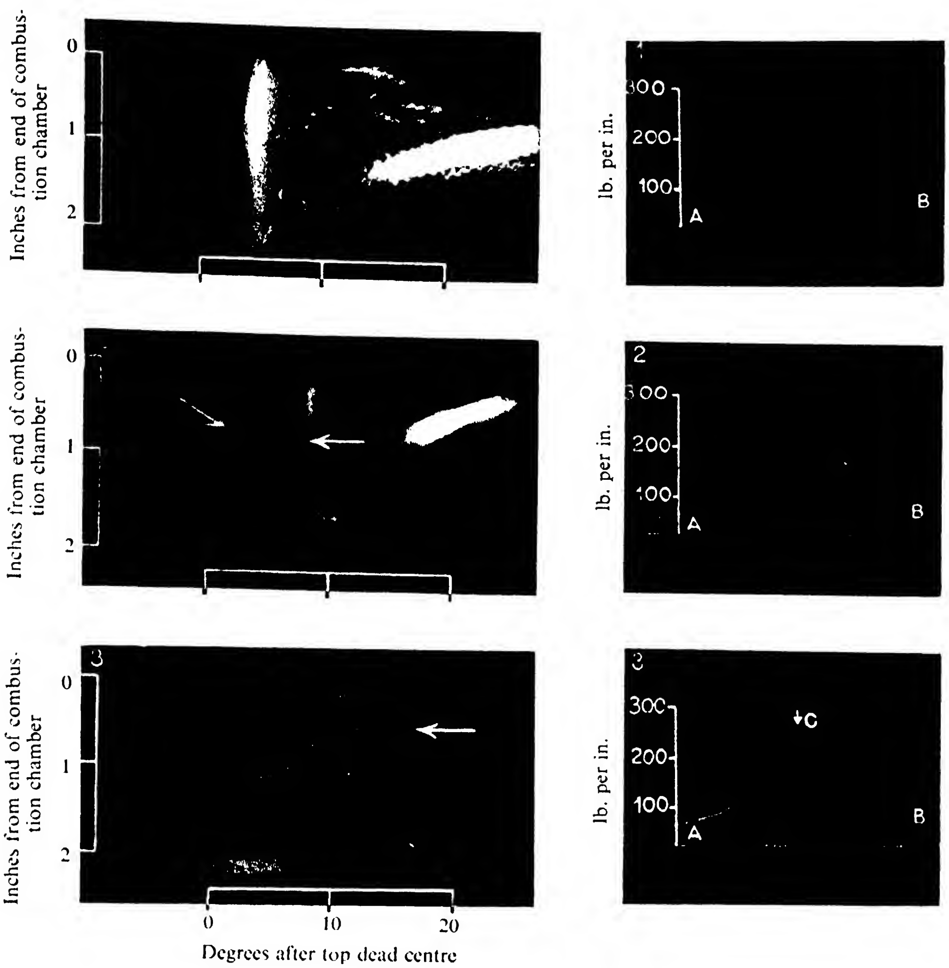


Fig 6

Flame photographs and pressure records showing various degrees of severity of knock

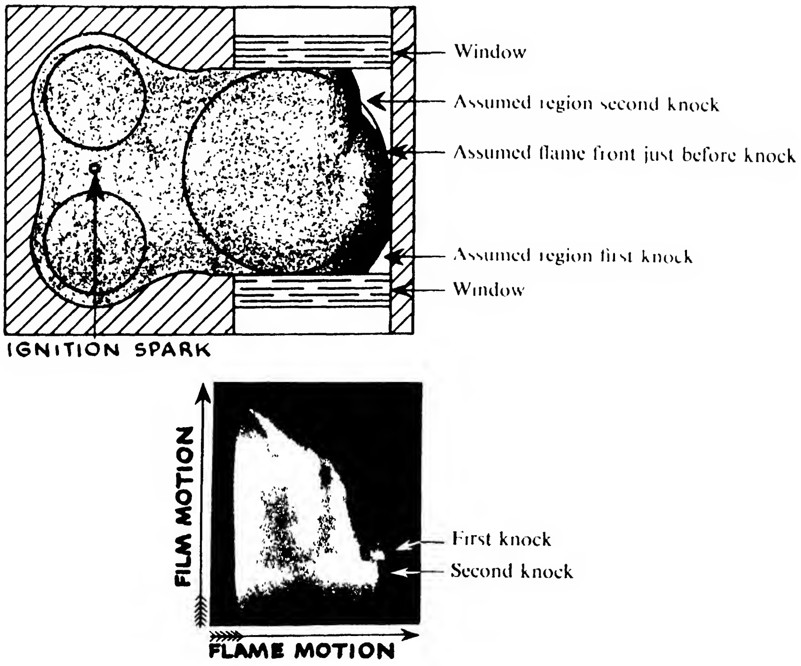


Fig. 7. Diagram showing how the portion of the charge which knocks may be separated into two parts

(*b*) The photosensitized reactions are interpreted similarly, but the initial atoms and radicals are provided by the method of sensitization which gives rise to H atoms, O atoms, or OH radicals, e.g. $Hg^* + H_2 \rightarrow Hg + 2H$.

(*c*) The heterogeneous reaction may be an actual chemical oxidation by some oxidizing agent, the mechanism of which would have to be separately investigated in each case, or it may be a reaction between oxygen and hydrogen adsorbed on the surface.

(*d*) Reactions which occur on the surface may give rise to products such as H atoms which can start a reaction chain, and in this way the homogeneous thermal reaction in the gas phase is probably started; for two streams of hydrogen and oxygen do not combine appreciably till much higher temperature unless a surface is present [1, 1930]. The chains probably start at the walls of the containing vessel and are also broken at the walls or by ternary collision in the gas. There is a critical pressure (at only a few millimetres pressure) below which at a given temperature the gases only react slowly, while above which instant reaction and explosion occurs, this region is bounded by an upper pressure limit, above which the reaction again proceeds at measurable rates [26, 1934].

These limit phenomena are explained by the branching of the reaction chains [56, 1935]. The velocity of reaction $v = N_0/(\beta-\delta)$, where N_0 is the number of reaction centres formed per second and β is the probability of the breaking of a chain and δ the probability of the branching of a chain. If $\delta \geq \beta$ then v becomes infinite and explosion ensues, and the lower pressure limit for explosion is reached when $\delta = \beta$. $(\delta - \beta)$ or ϕ is the net branching probability, and if it is greater than zero, the number of reaction centres will increase exponentially, $v = Ae^{\phi t}$ (where A is a constant and t is the time). If ϕ changes very rapidly, sudden explosion will occur for a very small change in conditions. The upper limit is explained by β becoming greater than δ, owing to breaking of the chains by triple collision in the gas phase; when $\beta > \delta$, the reaction is held in check in spite of branching and proceeds at measurable velocity. Ignition due to the branching of chains leads to a relation $\log p^m = A/T + B$ for the dependence of the lower pressure limit on the temperature, but this is no criterion of a branching chain mechanism, for the same kind of expression is obtained for a pure thermal ignition—an ignition which is occasioned by the heat of reaction being unable to be dissipated sufficiently rapidly to prevent self-acceleration of the reaction rate. The ignition of hydrogen in the low-pressure region is explained by chain branching, that at higher pressures and temperatures can probably be accounted for by thermal self-acceleration.

The kinetics of the hydrogen-oxygen reaction, as Hinshelwood has pointed out, can be interpreted if any chain-carrier X_O is formed which reacts with a molecule of hydrogen, thereby producing a chain carrier X_H which in turn reacts with a molecule of oxygen and regenerates the carrier X_O. Thus the chain scheme given for the photochemical reaction would be one which could satisfy the reaction kinetics of the thermal reaction: viz.

$$\begin{tikzcd}
O_2 + H \arrow[r] & HO_2 \arrow[d] \\
H_2O_2 + H \arrow[u] & HO_2 + H_2 \arrow[l]
\end{tikzcd}$$

where the hydrogen atom is X_H and HO_2 is X_O. Whether the hydrogen peroxide is formed and subsequently decomposed, or whether $H_2O + OH$ is formed in a single step is questionable. In the latter case $OH + H_2 \rightarrow H_2O + H$, and the chain proceeds. If the necessary energy is available (26 cal) $H_2 + HO_2$ may give $2OH + H$, and this will provide the chain branching feature required for the explanation of the low-pressure limit.

It is probable that the hydroxyl radical plays a predominant role at higher temperatures, while the carrying over of activation energy from one reaction particle to the next (energy chains) may also become an important factor in determining the rate at which the reaction proceeds above the upper pressure limit. There are quite a number of elementary processes possible, and it is by no means certain yet what are the most favoured reactions particularly in those cases where traces of other substances such as NO_2 are added and greatly affect the reaction rate. If this is so in the case of the simple hydrogen-oxygen reaction, exact knowledge of the more complicated hydrocarbon oxidation is further to seek.

There are a very large number of hydrocarbons and by no means do they behave similarly, for instance, methane is very resistant to oxidation compared with *n*-heptane, while neither the olefines nor the cyclic hydrocarbons behave in the same way as the paraffins, &c. Nevertheless there are certain general features about the combustion of hydrocarbons which make it possible to draw some general conclusions.

Investigations have been made by observing:

(*a*) Slow oxidation rates by flow methods or statically in bulbs.
(*b*) Absorption and emission spectra of burning hydrocarbons.
(*c*) Self-ignition temperatures under various conditions.
(*d*) Knock in engines.

Brief reference to some results of these four different methods of investigation will next be made.

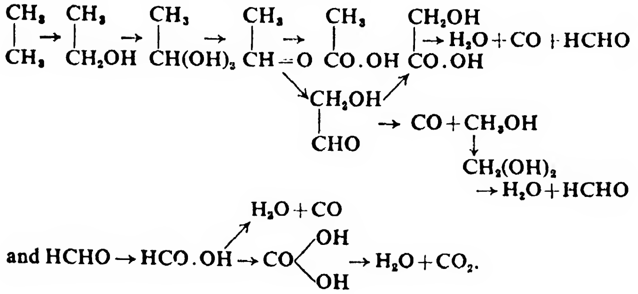
(*a*) Investigations on the slow oxidation of methane, ethane, ethylene, acetylene, propane, propylene, butane, butylene, pentane, hexane, octane, benzene, &c., have been carried out, sometimes by flowing the gases through a heated tube and then examining the products, sometimes by analysing the gases after heating in a closed bulb for different periods of time. It is not possible to give here detailed results of such experiments (cf. Article 3 and article by Newitt and Townend on 'Combustion Phenomena of Hydrocarbons').

There is a certain temperature at which each vapour will commence to oxidize fairly rapidly, but that temperature depends on the shape, volume, and material of the vessel, on the composition of the mixture and the rate of heating, &c. [32, 1927]. The reaction is generally preceded by an 'induction period', the length of which is influenced by the nature of the surface and a variety of circumstances and can even be eliminated by addition of small quantities of aldehydes, or greatly extended by the addition of inhibitors (e.g. lead tetraethyl). The actual reaction rate is also dependent on the surface of the vessel, and on the concentration of the reagents, and is influenced by the presence of accelerating or inhibiting agents, &c. The change of reaction rate with time provides an S-shaped curve, the velocity increases after the period of induction and then again falls off. The induction period which occurs in so many reactions, is explained, according to Semenoff, by the primary chain mechanism giving rise to an intermediate which in due course provides centres for the generation of the original chain; the branching factor δ is small and ϕ can therefore remain at quite a small value for some time before the exponential increase becomes considerable. The diminution in rate towards the end of the reaction is due to the diminished concentration of the original substance and therefore of its immediate products.

The characteristics of the reactions of hydrocarbon with oxygen or air are definitely those shown by systems of reacting substances which possess a chain reaction mechanism; for instance, the influence of inert gas, the effect of walls or surfaces, the effect of pressure, the effect of concentration of reactants, the induction period, the chemiluminescence, and the effect of inhibitors are all such as would agree with a reaction chain mechanism [50, 1932]. It must be borne in mind, however, that it is not only the oxidation of the initial hydrocarbon that occurs (as in the simpler case of hydrogen), but also the separate oxidation reactions of the various intermediate products, alcohols, aldehydes, &c., which are formed during the progress of the oxidation. A portion of these intermediate products may escape further oxidation and appear as final products; others may not survive.

The combustion has an autocatalytic nature [15, 1927], for some of these products are found to accelerate the reaction of the initial hydrocarbon and earlier products (cf. Articles 3 and 13). It is known, for instance, that acetaldehyde very markedly influences the induction period and slow combustion of ethane and even that of ethylene at the lower temperature at which it reacts. The same is the case for the higher hydrocarbons; for instance, valeraldehyde greatly affects the oxidation of pentane [50, 1932]. It is quite possible also that some of the products act in the reverse sense as inhibitors of the main reaction; phenols produced in the slow combustion of aromatic substances may have such an effect. Certain peculiarities regarding the combustion of benzene can be so explained.

The actual products of oxidation of these various hydrocarbons, alcohols, aldehydes, peroxides, acids, CO, CO_2, &c., have been determined in many cases with great care, and appear to fit the scheme already referred to, whereby the initial molecule of hydrocarbon is successively hydroxylated to give an alcohol an unstable dihydroxyl, an aldehyde, and an acid; e.g. for ethane:



$$\begin{matrix}CH_3\\|\\CH_3\end{matrix}\rightarrow\begin{matrix}CH_3\\|\\CH_2OH\end{matrix}\rightarrow\begin{matrix}CH_3\\|\\CH(OH)_2\end{matrix}\rightarrow\begin{matrix}CH_3\\|\\CH{=}O\end{matrix}\rightarrow\begin{matrix}CH_3\\|\\CO.OH\end{matrix}\qquad\begin{matrix}CH_2OH\\|\\CO.OH\end{matrix}\rightarrow H_2O+CO+HCHO$$

$$CH{=}O\searrow\begin{matrix}CH_2OH\\|\\CHO\end{matrix}\nearrow CO.OH;\quad\begin{matrix}CH_2OH\\|\\CHO\end{matrix}\rightarrow CO+CH_3OH\rightarrow CH_2(OH)_2\rightarrow H_2O+HCHO$$

$$\text{and } HCHO\rightarrow HCO.OH\rightarrow CO\begin{matrix}OH\\OH\end{matrix}\rightarrow H_2O+CO_2.\qquad HCO.OH\nearrow H_2O+CO$$

One criticism which has been raised against this hydroxylation theory is that since an aldehyde oxidizes more rapidly than an alcohol, the proportion of alcohol found in the products should be greater than that of the corresponding aldehydes, whereas at ordinary pressure the opposite seems to be the case. However, if the pressure is increased, the yield of alcohol becomes many times that of the aldehyde [45, 1932–3]. The variation of the proportion of alcohol to aldehyde with the pressure seems to indicate in the case of methane that the alcohol is formed by a reaction of higher order than the aldehyde and that the former is not therefore a primary product [28, 1935]. It may also be remarked that if an alcohol is the primary product of oxidation, if an inhibitor is used to delay the reaction and if it does so by destroying the effects of intermediates subsequently formed, then the inhibitor should have as great an effect on the oxidation of the alcohol as on that of the hydrocarbon; this does not appear to be so.

Be these criticisms justified or not, the theory provides a broad picture of the successive attack of oxygen upon the molecule, though it does not provide a detailed explanation of the kinetics of the reactions which occur (cf. article by Newitt and Townend on 'Combustion Phenomena of Hydrocarbons'; also Article 3).

According to Beatty and Edgar's experiments, in which heptane, octane, and various aldehydes were oxidized by a flow method, a terminal group of the hydrocarbon is first attacked by the oxygen forming an aldehyde which then gives CO and H_2O and the next lower aldehyde and so on down to the simpler products [2, 1929, 1934]:

$$RCH_3+O_2\rightarrow RCHO+H_2O$$
$$RCHO+O_2\rightarrow R^1CHO+CO+H_2O,\ \&c.$$

In accordance with this, aldehydes and water and a little CO_2 appear to be the first products detectable on passing a hydrocarbon through a heated tube, followed by the CO which is associated with the oxidation of the aldehydes; H_2O and CO_2 are the final products, the proportion of which increases with the temperature, but at the low temperatures many of the intermediate compounds are formed in quantity and escape combustion. Much depends on the initial composition of the mixture, and as a rule the 1 : 1 mixture is the most reactive, but the influence of excess of the combustible is greater than that of the oxygen, so that if the first step involves the encounter of a radical and oxygen, the second is probably the encounter of the resulting product with a hydrocarbon molecule.

(*b*) Spectroscopic studies of the intermediate products formed during the slow combustion of hydrocarbons have been limited to the determination of the emission bands from low-temperature luminescent flames [57, 1935] and to the identification of bands due to those molecules which can absorb light in convenient regions of the spectrum [18, 1933]. The luminescent flames from a variety of substances, hydrocarbons, olefines, ether, aldehydes, &c., all show similar band structure which may be due to formaldehyde, or to a radical of similar structure and sufficient life. The absorption bands provided by burning hydrocarbons prove that formaldehyde and organic acids are formed and possibly also organic peroxides; hydrocarbons from butane upwards give another band (about 2,600 A.). This band appears to be due to the formation of certain oxygenated ring compounds as secondary products [63, 1935]. Spectra of the high-temperature flames of burning hydrocarbons show the presence of OH, CH, and C—C radicals [6, 1928]. The luminosity which persists after the passage of flame seems to be due to the return of excited CO_2 to the normal state [70, 1931–2; 23, 1933]. This luminosity is greatly enhanced when compression waves pass through the products of combustion and increase the collision frequency and therefore the rate of return to the normal state. Observations of the infra-red spectrum of hydrocarbon flames have been made which indicate that most of the energy is radiated in bands due to CO_2 and H_2O molecules and some from continuous radiation from particles of incandescent carbon.

(*c*) Investigations of the ignition characteristics of hydrocarbons have been numerous and have led to interesting results. (Reference should be made to Articles 3, 5, 6, and 7.) No attempt will be made in this article to detail the ignition characteristics of the various hydrocarbons, but some general deductions about the character of their combustion which arises from a study of ignition will be made. The ignition of methane was studied by Dixon from 1,000 to 150 mm. pressure and by numerous other investigators. Neumann and Serbinoff [44, 1932] found three pressure limits for explosion, instead of two as for hydrogen, while for a higher percentage of methane the expression $\log p_m = A/T+B$ was followed down to quite low pressures.

Many vapours burn with a cool flame at temperatures far below their normal inflammation-point; hydrocarbons show this effect and fog formation due to fairly high-boiling liquid products [24*a*, 1928] often accompanies the phenomenon. Prettre [44, 1932], whose article in this series gives fuller details and references, has shown that there is a temperature at which luminescence becomes detectable, and then a region of temperature in which actual cold flames are visible and again another temperature beyond which no such flames are produced. Relating to these phenomena are those which Townend and his associates [62, 1931] have found in experimenting on the effect of pressure on the self-ignition temperature of hydrocarbons and on the extent of the region of cool flames (see Article 5). On letting hydrocarbon mixtures into a heated bomb, ignition may occur in a lower temperature region (250–350°) or at a much higher temperature (500–600°), depending partly on the composition of the hydrocarbon mixture, but mainly on the total pressure. Only methane appeared to ignite in a single high temperature region, all the other normal paraffin hydrocarbons could be brought to ignite in a much lower temperature region (250–350°), provided the total pressure was above a certain critical value. For the higher hydrocarbons more than one low temperature region was observed, but below a certain critical pressure only one ignition zone exists. Inhibitors tend to prevent ignition in the low temperature region, and so at a given pressure greatly increase the ignition temperature. The fall in the ignition temperature at a critical transition pressure corresponds with the incidence of knock in an engine on reaching a certain compression ratio. Benzene, 'iso-octane', alcohol, and methane do not ignite in the low temperature region and do not give rise to knock, and benzene and 'iso-octane' only with difficulty. The lag in ignition at these critical pressures is still quite considerable (approximately 1 sec.), but it is possible that at the higher pressures caused by regions of compression in front of the flame towards the end of combustion in the cylinder of an engine, that the lag might be reduced to as little as 0·001 sec. which is all the time available for ignition.

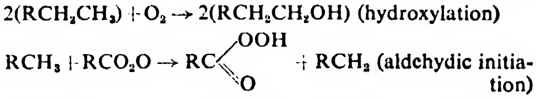
Townend has shown that the shape of the curve bounding the lower temperature region is closely connected with the ignition behaviour of acetaldehyde: the lower ignition range is related to the temperature region in which the maximum amount of aldehyde is formed. Pease [48, 1929] and also Beatty and Edgar [2, 1929, 1934] draw attention to the negative temperature coefficient of the rate of oxidation of certain hydrocarbons above the cool flame temperature region. Suppose then that A oxidizes direct to B with a velocity V_1, and suppose A forms an intermediate body X, and that $A+X$ react to give B with a velocity V_2; then since X is an intermediate product of oxidation, its maximum concentration will depend on the ratio of the velocity constant of the formation of X from A to that of destruction of X to give B, and if the concentration of $[X]_{\max}$ decreases with increase of temperature $v_2 = K[X]_{\max} e^{-E_a/RT}$, this will be small at low and high temperature, because of the smallness of $e^{-E_a/RT}$ in the one case and of $X_{\max}$ in the other; this provides a formal reason for the negative temperature coefficient which, as $e^{-E_a/RT}$ increases, again becomes positive (see Neumann and Aivazov [43, 1935]). The observations here briefly referred to show that the products of oxidation of hydrocarbons influence the course of the oxidation; the process is clearly an autocatalytic one. Not only do the products of oxidation of secondary products, such as acetaldehyde, affect the reaction rate, but it is possible that primary products may be formed (such as peroxides) which affect the rate, as suggested by the above formal representation.

It is significant that in spite of the many possible ways in which reaction might occur there is a remarkable similarity in the behaviour on oxidation of the hydrocarbons of a certain type (and also of the various classes of derivatives formed from them); whatever the process of oxidation is, it is probably very similar for the same kind of molecule even though the molecular weight may be very different. It is only methane and to a much less extent ethane that exhibit a rather marked difference; the higher straight-chain hydrocarbons (butane upwards) probably yield a great variety of subsidiary compounds due to ring formation, polymerization, &c., but the main characteristics of the oxidation remain very similar, and make it seem probable that the same mechanism is at work.

The initial step in the reaction is still unknown, various suggestions have been made, for instance, assuming the terminal group is first attacked:

Dissociation $RCH_2CH_3 \rightarrow RCH_2— + CH_3—$
$RCH_2CH_3 \rightarrow RCH_3 + CH_2—$
$RCH_2CH_3 \rightarrow RCH{=}CH_2 + H_2$
$RCH_2CH_3 \rightarrow RCH_2CH_2— + H.$

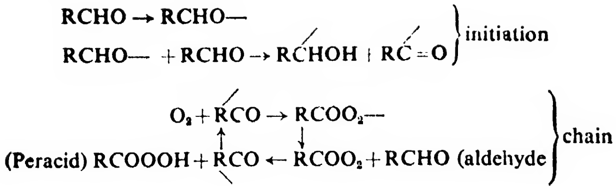
Oxidation $RCH_2CH_3 + O_2 \rightarrow RCH_2CH_2OOH \rightarrow RCH_2CHO + H_2O$ (peroxidation)
$2(RCH_2CH_3) + O_2 \rightarrow 2(RCH_2CH_2OH)$ (hydroxylation)



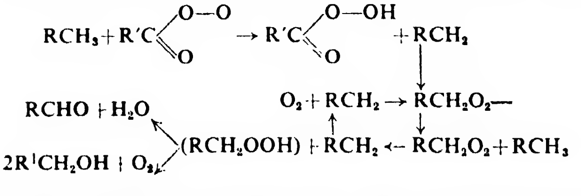
$RCH_3 + RCO_2O \rightarrow RC\overset{\diagup OOH}{\underset{\diagdown\!\!\diagdown O}{}} + RCH_2$ (aldehydic initiation)
$RCH_2CH_3 + O \rightarrow RCH_2CH— + H_2O$ (O atom initiation)
or $RCH_2CH_3 + O \rightarrow RCH_2CH_2OH.$

These do not exhaust the possibilities. Free methyl radicals are readily formed by pyrolysis of many hydrocarbons and their derivatives; there are almost sure to be some present. Free ethyl and propyl radicals have also been shown to be capable of existence for about 10^{-3} sec., but it is unlikely that higher radicals have an appreciable life. They probably give rise to hydrogen atoms, methyl radicals, and methane, ethane, and unsaturated hydrocarbons. As the C—C linkage is more readily broken than the C—H, the dissociation to give free methyl radicals is more likely than the splitting off of hydrogen atoms. The production of CH_2 radicals is perhaps more likely particularly at high temperatures than CH_3 as shown by Belchetz and Rideal [3, 1935]: while the least likely of all the first four processes is the direct production of the unsaturated hydrocarbon by the removal of a hydrogen molecule from either two different carbon atoms or from one carbon atom. There is, indeed, no evidence for the production of the ethylenic bond from absorption spectra experiments.

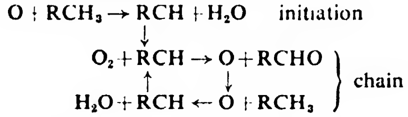
However, it is doubtful whether any of these dissociations is responsible for the initiation of the oxidation process which may take place due to one of the other processes. The oxidation of an aldehyde RCHO (in the liquid state) according to Backström takes place as follows:



The aldehyde can thus give rise to oxygenated radicals (like HO_2 in the case of the hydrogen oxidation) which could react as follows with a hydrocarbon and initiate a chain.



Thus aldehyde or alcohol can result as products of this chain reaction initiated through the radicals produced from aldehydes which may initially arise by reaction at the walls. The effect of aldehydes on the induction period is consistent with such a scheme of initiation. This scheme of oxidation is formally the same as that for the aldehyde and for hydrogen. Furthermore the peroxide RCH_2OOH, if any accumulates and is not at once decomposed, can disrupt to give hydroxyl radicals, which in turn can react with RCH_3 to give $RCH_2 + H_2O$, so that chain branching can occur in this way and lead to explosion; olefines, formaldehyde, &c., are produced by reactions which can occur alongside the main reaction. This scheme of oxidation has been given in detail by Ubbelohde [63, 1935], who has summarized in another article of this series the work that has been done on the slow combustion of hydrocarbons. Others view oxygen atoms in one way and another, as the chain carriers (Semenoff [57, 1935], Norrish [46, 1935]), and the kinetics of the oxidation of methane certainly fit in very well with this view. Norrish's scheme for higher hydrocarbons would be:



Branching and initiation of chains is provided in this scheme by oxygen atoms produced from the action of oxygen on an aldehyde.

$$RCHO + O_2 \rightarrow RCOOH + O$$

The alcohols are formed as a result of the destruction of the chain:

$$RCH_3 + O + M \rightarrow RCH_2OH + M.$$

Pease's investigations [49, 1935] on the oxidation of propane led him to conclude that the molecule of the hydrocarbon activated by collision combines with oxygen to form methoxyl (CH_3O) radicals which act as chain carriers. Pease and others have shown that considerable quantities of peroxides are formed but as the reaction-rate is not altered when the peroxides are destroyed by a KCl saturated surface, those peroxides isolated can hardly be the initial products of the reaction. There is, however, photochemical evidence for the primary production of peroxides, for instance in the oxidation of ethyl iodide [27, 1934] the kinetics are best explained by the initial formation of an active peroxide $C_2H_5O_2$, which then reacts with a further molecule of ethyl iodide to give acetaldehyde, ethyl alcohol, and iodine.

Although it would be generally agreed that in the oxidation of a saturated paraffin reaction chains are operative, there is as yet no agreement on the mechanism of the process or the nature of the chain carriers. The same remark applies to the olefine hydrocarbons, for instance, Bone and his associates have carefully investigated the products formed during different stages of the combustion of ethylene and conclude that successive hydroxylation accounts for the results obtained, ethylene oxide being formed from the vinyl alcohol which is considered as the primary product. This interpretation is not in complete agreement with certain other investigations which require the primary formation of a peroxide by the addition of oxygen (*vide* Thompson and Hinshelwood [61, 1929], Lenher [30, 1931], Norrish [46, 1935], Lucas, Prater, and Morris [35, 1935]).

It is questionable whether the reaction mechanism is similar in the case of olefines to that of the paraffins until the length of chain overcomes the effect of the double bond. Pidgeon and Egerton [50, 1932] did not find that amylene accelerated the slow combustion of pentane though hexane had such an influence, and the chemiluminescent effects with the olefines are much less marked. The influence of the combustion of one hydrocarbon upon that of another throws some light on the mechanism of their reactions (cf. Mardles, Article 13).

These facts stand out clearly, viz. that there is a difference in behaviour at normal pressures between the higher paraffin hydrocarbons on the one hand and the lower on the other, and that there is some autocatalytic effect of the products which influences the oxidation of the higher hydrocarbons, whereas the effect is not pronounced with the lower hydrocarbons unless the pressure is increased. It is also clear that the combustion of different hydrocarbons has much in common, pointing to a similarity of mechanism.

(*d*) The remaining group of investigations which has been used to throw light on the way hydrocarbons commence to burn is more directly connected with investigations on knock in engines.

An extensive series of measurements (particularly in the laboratories of General Motors Ltd., Detroit) has been made of the knocking characteristics of various pure hydrocarbons. Many substances are too scarce to be tested in the engine in the pure state and it is necessary to make blends with other fuels, but using a standard fuel with which to blend the other substances, it is possible to compare their relative behaviour in the blended fuel. Measurements have also been made on the pure substances by determining the pressure at which knock first becomes audible (critical compression ratio). The results obtained are summarized in the article by Campbell and Boyd of this series. As already pointed out it would hardly be expected, considering the complexity of the processes of hydrocarbon combustion, that the ratio of the figures obtained for the knock-rating of two different hydrocarbons in a certain engine under specified conditions would be the same for another set of conditions or in other engines where different temperatures, time pressure, and surface conditions prevail, and this is still less to be expected for a blended fuel, for one hydrocarbon will influence the burning of the other somewhat differently. Furthermore, what is the precise significance that can be attached to the incidence of knock of a degree of intensity measured by the knock-meter or the ear?

In spite of these shortcomings relating to the method of knock measurement, there are very definite relationships between the figures obtained for the different compounds investigated.

As a general rule, for all types of hydrocarbon a straight chain of CH_2 groups knocks the more, the longer the chain; while any break in the chain of CH_2 groups produced by branching of the molecular structure, or by double bonds, tends to raise the knock-rating. The more compact the structure of the molecule, the higher is the knock-rating.

In a mixed fuel, the paraffinic straight-chain constituents knock most, the aromatics and olefines least, the naphthenic constituents being intermediate in their behaviour. The diolefinic constituents and certain unsaturated cyclic compounds are apt to polymerize easily (particularly in presence of the oxygen of the air) and give rise to 'gums'.

In a series of compounds with six carbon atoms the aniline equivalents (see p. 3008) are given as follows:

Hexane	−6
Cyclohexane	7
1,2-Hexene	8
Cyclohexadiene	10
Benzene	10
2,3-Hexene	12
2,3-Dimethylbutane	19

and these figures serve to illustrate the general effect of the constitution on the knock-rating. It will be noted that the saturated paraffin, 2,3-dimethylbutane, has the highest knock-rating, but that the isomeric straight-chain paraffin has the lowest.

In a ring compound the more alkyl groups attached to the cyclic compound, the more the substance knocks, thus 1,3,5-trimethylcyclohexane knocks more than 1,3-dimethylcyclohexane. Doubling the ring increases knock. A double bond is protected from oxidation by substitution in the neighbouring carbon atom and the knock-rating increases. A double bond in the centre of the chain is much more effective than one near the terminal groups, for the reason that the longer the chain of CH_2 groups the greater the knock. Similarly, two double bonds give higher ratings than one, though tendency to polymerize becomes greater. The double bond is much less easily broken than the C—C or C—H linkages.

It has been suggested by Rice [55, 1934] that the knock-rating of a hydrocarbon molecule depends on the ease with which it can split off methyl radicals, but it is possible that the same attributes which make disengagement of methyl radicals easy, also make attack by oxygen easy, not necessarily that the process of oxidation is initiated by the dissociation of the methyl radicals from the remainder of the hydrocarbon without the intervention of any other initiating mechanism.

The knock-rating is related with the stability, with the oxidizability and more particularly with the ignitability (in the low-pressure range) of the fuel. Figures which illustrate this connexion are given in Article 4 on 'The Susceptibility to Oxidation of I.C. Engine Fuels'. The ignition temperature decreases and the oxidizability increases with the molecular weight, in the same manner as the knocking tendency of a hydrocarbon (cf. Article 6, 'Spontaneous Ignition Temperatures').

It has been possible to study the combustion process in a petrol engine by sampling the gases from an engine cylinder at any moment in the cycle at which it is desired to withdraw them. Analyses not only of the final gaseous products [69, 1930; 19, 1935], but of the amount of intermediates (such as aldehydes, &c.) which are formed, have been made. Formaldehyde is obtained in very appreciable amounts (e.g. 1 vol. in 200) together with higher aldehydes usually in smaller quantity. These commence to be formed prior to the arrival of flame at the sampling-valve, and the amount formed is appreciably greater in knocking explosions. Formaldehyde in very much diminished amount can be detected in the burnt gases but no other aldehydes. These results agree in most particulars with observations of the absorption spectra of gases in the knocking-zone in an engine by Whittrow and Rassweiler [71, 1933]; the absorption due to formaldehyde is clearly visible in the regions ahead of the advancing flame, and there are indications of the presence of other products which absorb light in the ultra-violet region.

By sampling in every alternate cycle, it has been possible to show that aldehydes are formed in the compression stroke when no flame is present, but the amount is very much greater when flame is present [65, 1935]. A large part of the slow combustion observed, therefore, must be due to the proximity of the flame and occasioned by the high temperature and pressure to which the gases are exposed (or possibly by the active radicals which are projected from the flame into the unburnt gas ahead) and not due in the main to the hot surface of valves, &c., though these no doubt contribute to the production of a certain amount of precombustion (p. 2916). Peroxides have also been found in the products of combustion of engines by Callendar and Mardles [8, 1927] and by Dumanois, Mondain-Monval, and Quanquin [12, 1931].

The addition of pro-knocks to fuels is particularly instructive. Isopropyl nitrite, ethyl nitrite, &c., have been known for some time [7, 1924] to act as powerful knock-inducers or 'pro-knocks'. It has been found that the quantity needed to give rise to audible knock is only of the order of 1 mol. in 10^5 mols. of the gaseous charge in the cylinder. It has also been found that peroxides such as diethyl peroxide, ethyl hydrogen peroxide, or acetyl peroxide are as effective if not slightly more effective than the nitrates and nitrites as knock-inducers [19, 1935; also 8, 1927]. It is known that fuels which become peroxidized increase their tendency to knock, and that the lead susceptibility decreases also with the peroxidation of the fuel. The peroxides found in such fuels are mainly olefine peroxides which are, however, not very strong pro-knocks.

The alkyl, alkyl hydrogen, or aldehyde peroxides are the only known class of substances which might be formed as products of the oxidation of hydrocarbons which when added to fuels in very small quantity will give rise to knock; aldehydes knock violently, but when added to fuels it requires 100 times as much aldehyde as peroxide for the same degree of knock to be produced. Alcohols relatively do not knock at all. Many peroxides (olefine peroxides, &c.) have only a weak effect as compared with these other types of peroxides. It appears that only those substances are effective which would disrupt to give —OR, and possibly —OH radicals, and it has been suggested [64, 1935] that these radicals set up branching reaction chains and so give rise to an enhanced rate of combustion. Ethyl nitrate and nitrite have been shown to decompose in such a way [58, 1934], and as nitrogen peroxide itself was found to produce relatively little knock, the —OR radicals or other radicals produced by alkyl peroxides and nitrites, &c., seem to be responsible.

It was found that when either acetyl or ethyl hydrogen peroxides were added to fuel that the peroxides could be recovered quite late in the compression stroke from the sampling-valve, so that these substances are capable of surviving the compression stroke.

A certain quantity of nitrogen oxides (about 1 mol. in 10,000 mols. of the cylinder gases) are formed during combustion in the engine. They are formed in greater quantity the greater the knock but they are not responsible for knock, for many fuels which do not knock give rise to even greater amounts than fuels which do knock.

In spite of the presence of nitrogen peroxide, it has been found possible to detect organic peroxides in the gases extracted from the sampling-valve at the moment just prior to knock [19, 1935]. They have also been obtained when an engine is motored at high temperature [12, 1931]. These peroxides behave towards reagents not like acetyl peroxide but rather as the alkyl hydrogen type of peroxide and are present in an amount (1 in 10^5) nearly as great as would give rise to the same degree of knock if added to the fuel; even so the amount is very small and near the limit of detection.

It has been mentioned that during the combustion of the higher hydrocarbons (butane, &c.) peroxides are formed in considerable quantity in the regions of temperature just below the lower pressure ignition when cool flames occur [40, 1931]. These peroxides were thought to be alcoxyperoxides (formed from formaldehydes and alkylhydrogen peroxides, &c.), but Ubbelohde [63, 1935] searching for the absorption band found by Egerton and Pidgeon [18, 1933] in the oxidation of hydrocarbons identifies some of them with peroxides of oxygenated ring-compounds (vinyl-ether peroxides of hydrogenated furans and pyrans), which are formed from peroxidized radicals of the hydrocarbon (R—O—O) or from R—O—OH. These peroxidized products formed in the slow combustion, however, do not promote knock to any great extent like acetyl peroxide, ethylhydrogen peroxide, or diethylperoxide do under similar circumstances. The peroxides obtained from the engine may well be these vinyl ether peroxides rather than any primary peroxide like R—O—OH, which if formed at all may be too quickly destroyed to be isolated. Nevertheless, whether primary products or not, the fact that organic peroxides are formed prior to knock is important, as it provides further clues as to the mechanism of the combustion of the higher hydrocarbons.

Although in these engine experiments, aldehyde peroxides (particularly acetyl peroxide) were not detected or isolated, they might be the compounds which are responsible for the incidence of knock. The amount of aldehyde (between 5 and 10% by volume in the fuel) which has to be added to a fuel to cause knock and the amount of acetyl peroxide needed (0·05%) were known, but it was found that the amount of aldehydes present (other than formaldehyde, which does not give rise to knock) was never more than about a quarter of the concentration needed to give rise to the concentration of acetyl peroxide necessary to cause knock. Consequently it was argued that other peroxide substances must be present which give rise to knock besides acetyl peroxide [65, 1935]. It is possible the argument may not be valid, if the concentrations as determined in the sampled gases are not truly representative, and that there are higher local concentrations of aldehyde in certain places within the cylinder. But there are other reasons for considering that acetyl peroxide is not alone responsible for knock, for larger percentages of acetaldehyde are obtainable from the combustion products of fuels which do not knock so readily as those that yield less acetaldehyde.

It has been found that diethylperoxide does not set up knock in an engine using hydrogen as fuel, whereas nitrogen peroxide causes knock [19, 1935]. These facts, contrary to what is experienced in an engine running on petrol, require further confirmation and study, but they indicate that the radicals which are responsible for knock with hydrocarbons are not the same as those which promote the combustion of hydrogen and therefore are not so likely to be either H or O atoms or —OH radicals.

Summarizing briefly the result of these various investigations on the combustion of hydrocarbons which have been classified on p. 2917 under headings (*a*), (*b*), (*c*), and (*d*), the kinetics of both photochemical and thermal oxidations indicate that a chain-reaction mechanism functions, the precise nature of the chain-carriers is not known, but there is some evidence of a similarity with the oxidation in simpler systems, such as with the oxidation of hydrogen. Stable products formed as a result of the chain are alcohols or aldehydes (in accordance with the indications of the hydroxylation theory), these substances also oxidize by chain-reactions, and their products can initiate the hydrocarbon chain-reaction so that the process becomes autocatalytic. Combustion seems to commence by the oxidation of the terminal CH_3 group of the longest structural chain, and the molecule which thus becomes attacked is probably rapidly oxidized down to final products of small molecular weight.

Experiments on the kinetics of the reaction and on ignition both indicate that there are two regions of oxidation, the low temperature region, and a higher temperature region. The mechanism is somewhat different at the lower temperature and it appears that a product is formed, the subsequent decomposition of which at a slightly higher temperature accelerates the oxidation and gives rise probably to branched chain-reactions or possibly to local release of thermal energy, which cause the ignition. The investigations on knock in engines indicate that the same causes that give rise to ignition in the low temperature region give rise to knock, and there is much evidence from these experiments that peroxides are the substances which are formed and subsequently in decomposing produce the sudden enhanced rate of combustion. There is evidence also that the aldehyde peroxides are not alone responsible for this, but that other peroxidized products are present.

In the higher temperature ignition region the combustion is similar to that occurring with methane and the chain-carriers, though formed perhaps by a similar mechanism, may behave differently than they do in the lower temperature region, where the temperature is not too high to allow traces of peroxides or some such products to exist which cause the sudden increase in reaction rate in the manner which has been suggested.

Anti-knock behaviour.

Reasons have already been adduced for hydrocarbon combustion being of a chain character; were this not so, it would be difficult to explain the action of inhibitors, very small quantities of which are needed to stop reaction. For 1 atom of lead in 200,000 mols. of fuel mixture could make very little difference to the rate of combination of hydrocarbon and oxygen molecules, if the rate was simply dependent on their mutual encounter; on the other hand, if each initiating particle was able to bring into combination a large number of other molecules by a chain-reaction, the destruction of the particle or the stopping of the chain at an early stage would make a great difference to the reaction rate. It would be expected too that if the amount of inhibitor was insufficient or the conditions of pressure or of oxygen concentration were such that too many chains were starting in a given time for their effect to be stopped, that the inhibitors would have very little effect on the rate. This is illustrated by the facts that in oxygen, lead tetraethyl at normal pressures in an ignition apparatus is ineffective, whereas in air it raises the temperature of ignition very greatly. Also, in Townend's experiments, it is found that the effect of the lead in varying the ignition from the lower to the higher region is very great in the neighbourhood of the critical pressure for ignition, but at higher pressures the ignition-point is very little raised and remains in the lower region of temperature.

It is also found from the behaviour of fuels in engines that certain minimum percentages of lead are needed to have an effect and that after a certain addition, further addition has less effect. These results seem consistent with the explanation that the inhibitor controls the number of centres from which reaction spreads.

The effect of lead tetraethyl in preventing knock was discovered by Midgley [39, 1920]. It was known that in a knocking explosion the intensity of the light of the explosion in the ultra-violet appeared greater than in the normal explosion, and in an attempt to absorb the ultra-violet and thereby prevent its possible effect in accelerating the explosion, halogens were tried, but as the effect on knocking of chlorine and iodine were contrary to each other, the idea was not promising, but it nevertheless led to trying other substances in neighbouring groups of elements. Diethylselenide and diethyltelluride were both found to be anti-knocks, and the organo-metallic derivatives of the next group, tin tetraethyl and particularly lead tetraethyl were found still more effective.

Lead tetraethyl was and still is the most useful anti-knock; only about one part by volume in about 1,300 of fuel is used, and as the bromide is volatile, addition of bromine compounds (ethylene dibromide) prevents the accumulation in the cylinder of products from the combustion of the lead. An anti-knock dope containing both ethylene dibromide (about 35%) and lead tetraethyl (about 62%) called 'ethyl fluid' was manufactured and is now used in large quantities for the improvement of motor fuels. An article of this series is devoted to the methods of preparation and analysis of the dope and another to the lead susceptibility of various fuels, so that it is unnecessary to give here further details of these matters. The lead susceptibility which is the rise in octane number produced by 1 c.c. of tetraethyl lead per U.S. gal. of spirit varies very much for different fuels; and as a general rule, the better the fuel, the greater the lead susceptibility. Lead ethyl is also somewhat more effective at high cylinder jacket temperatures.

At one time some trouble was caused by the attack of engine valves on account of the presence of ethyl lead in the fuel; this trouble has been largely overcome by the use of 'stellited' valves and other means [1*a*, 1934].

A number of other substances have been tried as dopes. Only certain nitrogen compounds (amines and imines) [7, 1924], phenols, quinone [64, 1935], &c., were specially effective amongst organic compounds, but about one hundred times as much of these are needed for the same effect as a similar volume of tetraethyl lead provides.

The iron and nickel carbonyls $Fe(CO)_5$ and $Ni(CO)_4$ were found very effective, but both are attacked by light and particularly the latter by moisture, and neither give volatile compounds easily removed from the cylinder, so that they are not so suitable as the lead compound. Sims and Mardles [56*a*, 1926] prepared organo-sols of lead, iron, and nickel which were effective as anti-knocks: slight effects were obtained with cerium xylyl and chromium phenyl.

It was shown by Weerman [66, 1927] that the anti-knocks raise the ignition temperature of petrol when a stream of air is blown gently through an ignition-pot (cf. Article 6). Egerton and Gates [17, 1927] found what metals affected the ignition-point, using either the vapours from an arc or from the heated metals and then sorted out the effective metals from the others. Potassium was found very effective, but sodium practically ineffective. Thallium was found more effective than lead. Manganese and Bismuth were the only other metals found appreciably effective. Since then experiments have been made in the engine from which the following estimates of effectiveness were made [19, 1935]. (See Article 11 by G. Calingaert and Article 13 by E. Mardles in this series on anti-knocks.)

	Relative efficiency on weight basis
Lead . .	1
Thallium .	11
Potassium .	4
Selenium .	0·07
Aniline . .	0·02

As potassium was so effective and as thallium was only effective when introduced along with air, it seemed that these metals were effective when in an oxidized condition. Similar experiments with lead in the ignition-pot pointed to the same conclusion. It was noticed, too, that those metals were effective for which the lower and higher oxides were in a state of equilibrium at temperatures about 300° to 400°. It thus appeared probable that one of the oxides is taken to a lower (or possibly higher) state of oxidation by encounter with the chain-carrier of the initiator of the hydrocarbon oxidation, and that the required oxide is then regenerated by further collision with oxygen molecules: it would be difficult to explain otherwise the effect of potassium and the lack of effect of sodium.

The organic anti-knocks such as aniline are themselves burnt and consumed, so that the latter class of anti-knock is not regenerated and is far less effective. The organic anti-knocks like aniline have been shown by spectroscopic means to decrease the amount of formaldehyde formed, whereas lead ethyl does not appear to do so to the same extent, so that probably their function is different [71, 1933].

If the anti-knock is in the form of small particles and not in the form of vapour, it is obvious that it cannot be so effective in reacting with those molecules or radicals responsible for initiating the chains. The metal must first be formed as vapour and then the molecules of metallic vapour oxidized [17, 1927]. It is found, indeed, that PbO from an arc and iron oxide from $Fe(CO)_5$ is practically ineffective when introduced as a mist of particles [19, 1935]. This fact may account for some of the discrepancies about the matter existing in the literature.

The kinetics of decomposition of lead tetraethyl and of nickel carbonyl have been studied, and it has been shown that dissociation into atoms and radicals (e.g. C_2H_5) occur and that the reactions are unimolecular. In agreement with this, it was found that $PbEt_4$ can act under certain circumstances as an initiator of chains and can accelerate the combustion of a hydrocarbon (e.g. pentane), but only if there is no oxygen initially present; a small trace of oxygen prevents such an action, so that presumably it is PbO or PbO_2 in the molecular state that has the pronounced anti-knock effect. Yet against this it must be mentioned that in the engine in the region of knock only Pb lines in the absorption spectra were observed and none due to PbO [53, 1935].

The speed of uniform rapid flame may be very little affected by the anti-knock; though the travel of slow flames of methane, of CO, &c., and hesitating vibratory flames are much affected [16, 1927; 14, 1929]. It seems that if the lead ethyl is decomposed and oxidized it is effective, but that unless it has time to react with and prevent the formation of reaction centres (chain initiators) it is comparatively ineffective. The behaviour of an anti-knock is dependent on the oxygen concentration, lead tetraethyl has no effect on the ignition temperature of petrol in oxygen (at ordinary pressures). The effect of an anti-knock varies also with the nature of the fuel on which it operates; this may be accounted for partly by the time available for decomposition of the anti-knock molecule which would alter with the rate of combustion of the fuel, and partly by the nature and amount of the intermediate products formed which will alter the number of chains which the anti-knock has to prevent becoming effective. It is remarkable that an anti-knock has apparently little effect in preventing the combustion and ignition of an alcohol, whereas it has a marked effect on an aldehyde and a hydrocarbon; since aldehydes are formed in the combustion of the alcohols, this would indicate that there are primary products in the oxidation of a hydrocarbon which are prevented from developing reaction-chains, as well as the products from the oxidation of the aldehyde. Further investigations, however, are needed to settle whether the anti-knock plays this double role.

Townend [62, 1933] has shown that under pressure the anti-knock has a much more marked effect in the 'critical' pressure region than at lower or higher pressures. The anti-knock, therefore, does not much affect the travel of the flame except in the region where the pressure is rapidly rising towards the end of travel of the flame; there its effect is very great. The effect of the anti-knock is probably due to the prevention of the development of explosive combustion caused by secondary products such as aldehyde peroxides, but whether it acts only on the aldehyde or also on the first stage of combustion of the hydrocarbon and hence decreases the amount of the aldehyde formed has yet to be established. Pro-knocks provide reaction centres just as anti-knocks destroy them, their effect is contrary; it is significant that the concentrations at which they become effective are approximately the same.

The use of anti-oxidants for the stabilization of fuels on storage and for other purposes is dealt with elsewhere in this series of articles (cf. Article 13).

Flame Propagation and Knock.

Flame propagation can now be reviewed having in mind the processes of slow combustion which have been discussed.

Whatever the nature of the gas, during the stage in which the cold unburnt gas ahead of the flame is being heated up, oxidation must be taking place to a more or less extent. The molecules are receiving energy by collision with molecules of already burnt products, or with molecules of diluents heated by the reaction or by collision with other unburnt molecules which have already received energy in such manner. It is not merely a question of thermal conduction, for some of the already burnt products will be molecules, atoms, or radicals, which are activated to varying extent and may be capable of reacting with a sufficiently active molecule of the unburnt substance or of activating it so that it will react on meeting with another radical or possibly with a molecule of oxygen. It then gives rise to products which may or may not propagate a chain.

In an ordinary flame, under conditions in which the density of the mixture presenting itself to the flame is constant, the velocity of propagation will be controlled by the change in the concentration N_c of combustible gas (dN_c/dt) and by the temperature gradient (dx/dT) in the reaction zone, thus

$$V = \int_{T_1}^{T_2} -\frac{\partial N_c}{\partial t}\cdot\frac{dx}{dT}\cdot dT,$$

where V is the volume of unburnt combustible entering the reaction zone per sec., T_1 is the initial temperature, T_2 the temperature of the burnt gas, and t, the time. From a knowledge of the kinetics of the reactions $O_3 \rightleftharpoons O_2+O$ and $O+O_3 \rightarrow 2O_2$ and of the diffusion coefficients, B. Lewis and V. Elbe [33, 1934] have attempted the determination of the velocity of the flame of ozone decomposition and the thickness of the flame zone, using also an assumption that the sum of the thermal and chemical energy per unit mass of the gas remains constant in the unburnt layer at T_1, and in the burnt layer at T_2. They point out the connexion between their method of approach to the problem of the calculation of flame-speeds and that of former investigators (e.g. [47, 1915]) which were based on the general equation

$$\frac{dH}{dt} = C_m\frac{dT}{dx} - K\frac{d^2T}{dx^2},$$

where H is the thermal energy liberated by the reaction, C_m is the specific heat of the mixture of gases, and K the thermal conductivity and into which there had to be introduced an indefinite temperature T at which the gases are brought to ignite. They show that formally there is no real difference, but by their method it is possible to make use of more or less precise knowledge of the reaction kinetics to replace the use of an indefinite ignition temperature. Unfortunately it is a matter of considerable complication to determine the integral

$$\frac{dN_c}{dt}\cdot\frac{dx}{dT}\cdot dT,$$

even in the comparatively simple case of ozone decomposition; furthermore, simplifications have to be introduced to avoid effects which no doubt exist due to loss of heat and change of conditions at the walls of the containing vessel. It cannot therefore be said that even in very simple cases that the flame velocity lends itself readily to calculation; though the outlook on the problem has been considerably modified by appreciation of the influences which the rate of reaction and the diffusion of the active products have upon the temperature gradient in the flame zone between the initial temperature and the maximum temperature of flame.

If the vessel into which the flame penetrates is closed so that the pressure increases, the collision frequency of the active products with unburnt gas is increased and so the velocity of the flame accelerates. Since the diffusion of the active products plays so important a part and since only a fraction of the number of unburnt molecules of combustible gas is effective, any slight irregularity in the density of the gas mixture may result in a local difference in flame velocity which immediately brings about conditions which produce a vibratory flame. By decreasing the effectiveness of reaction between active products and unburnt gas, flame can be slowed down; for instance, the writer has shown that one thousandth part of iron carbonyl nearly halves the velocity of flame of 50% CO/air. Clearly, so small a quantity of iron carbonyl could not affect the flame velocity unless the reactions started by the comparatively few effective collisions with active products were chain reactions; similar results have been obtained with methane mixtures.

(Another example of the importance of the reaction kinetics on the velocity of flame travel is the effect of small diameter tubes in preventing explosion which seems to be not so much dependent on the thermal conductivity of the material of the tubes, as on the effectiveness of the surface for breaking the reaction-chains.)

An accelerating flame may give rise to detonation in a certain mixture of combustible gas. The detonation can be made to occur at quite a definite position in the tube; though it depends not only on the composition of the mixture but on the various conditions such as the diameter of the tube and the initial pressure. Why the detonation is initiated is not precisely known. Berthelot and Veille suggested that the velocity of the explosion wave depended on the mean velocity of translation of the molecules of the products, supposing them to retain the reaction heat. This long abandoned idea has been revived in modified form in the theory put forward by B. Lewis [31, 1930].

The chain-carrier is supposed to receive reaction energy in the form of translational energy and to provide sufficient activation energy in this way to the molecules of combustible gas with which it collides, nearly every collision being therefore fruitful in starting another chain. The velocity of the detonation is then only limited by the translation velocity of the chain-carriers. This theory alone does not explain how it is that the mixture detonates suddenly even though, as in some cases, flame was being propagated previously at a fairly constant rate. Experiments have shown that when the flame encounters a wave of compression, that conditions for the setting up of detonation arise and the effects of pressure on the velocity of reaction being of a high order may account for the sudden enhancement of the collision efficiency.

The setting up of knock and of detonation differ in several particulars. The outstanding features of the former are the presensitization of the charge by reactions which have previously occurred or by the addition of small quantities of sensitizers and the prevention of such presensitization by inhibitors; detonation, on the other hand, is apparently unaffected by such sensitization or by inhibitors.

There is very little doubt knock and the low-temperature ignition of hydrocarbons are brought about by the local enhancement of the rate of reaction owing to a great increase in the number of chains started in a certain small region owing to the existence in that region of intermediate products which on the arrival of flame are decomposed. If the decomposition of these products give rise to a branched-chain reaction, there may be very rapid development of the reaction to explosion; the alternative suggestion that the reaction due to the exothermic decomposition of those substances lead to the thermal development of the explosion, seems less likely, but these two alternatives have to be further investigated. The effect of pressure in bringing about conditions for knock and for ignition at low temperature probably cannot be accounted for simply by reason of its effect on the reaction velocity, but is mainly due to its favouring the existence of the intermediate products. The identification of these products with the aldehyde peroxides and possibly with other peroxides, formed in an earlier stage of the oxidation, the presence of the latter being suggested by the different behaviour of the alcohols and olefines on the one hand and the paraffins on the other, has already been discussed.

In the petrol engine, flame starting from the spark and assisted by the turbulence of the gas travels rapidly through the disk-shaped space; the pressure rapidly rises, and the last part of the gas remaining unburnt is exposed to fairly extreme conditions, partly owing to rise of temperature due to the rapid rise of pressure and partly to the heat received from the walls and by radiation from the flame. The temperature may rise locally to above 500°, and there may even be time for self-ignition to occur before the flame reaches the gas (as shown by some photographs.) Owing to the pressure and temperature conditions the gas is presensitized, and when the flame reaches this region, the sudden increased rate of combustion is sufficient to set up intense compression waves which provide an explanation both of the vibratory pressure records obtained in knocking explosions, and of the waves seen reflected back and forth in the photographs of knocking explosions.

In the compression-ignition engine conditions are rather different, the fuel injected into the combustion chamber or cylinder, is exposed to rather similar conditions of pressure but the temperature conditions may be less severe as there is no flame from which the gases receive heat. During the ignition delay period, substances are formed which eventually give rise to the low-temperature ignition, and since the same processes produce the low-temperature ignition as produce knock, the pressure rise is rapid enough to produce compression waves and these lead to a knocking sound. But ignition starts in that region where precombustion is most advanced, and as the spread of flame is very rapid the rest of the gas is probably burnt up before any of these substances which lead to sudden *local* enhancement of reaction rate can accumulate, and the main explosion is usually fairly smooth. This is not so, however, with a poor fuel when the knock may become very pronounced. On this view, the relation of the cetene number and octane number of a fuel already maintained can readily be interpreted. The longer the delay, the more aromatic the fuels, the greater the tendency to rough and noisy running.

A number of different matters which relate to the study of knock have been briefly referred to in this article, but many of them are dealt with in a more comprehensive way in other articles of the series. Overlap between one article and another is inevitable, the more so as the phenomena of knock becomes explicable on lines which are becoming more generally accepted. Even though there may be some restatement, the differences in point of view by different workers and the experimental results which do not always quite accord are perhaps more valuable than the agreement as to the underlying explanations, for the reader can derive therefrom knowledge as to where further work is needed.

REFERENCES

1. Alyea, H. N., and Haber, F. *Z. physikal. Chem.* **10**, *B.*, 193 (1930).
1*a*. Banks, F. *J. Roy. Aero. Soc.* **38**, 309 (1934).
2. Beatty, H. A., and Edgar, G. *J.A.C.S.* **51**, 1875 (1929), and **56**, 102 (1934).
3. Belchetz, L., and Rideal, E. K. *J.A.C.S.* **57**, 1168 and 2466 (1935).
4. Bone, W. A., and Fraser, R. P. *Phil. Trans.* **230** A, 363 (1931).
5. Bone, W. A., Fraser, R. P., and Wheeler, W. H. *Phil. Trans.* **235** A, 29 (1935).
6. Bonhoeffer, K. F., and Haber, F. *Z. Phys. Chem.* **137**, *A*, 263 (1928).
7. Boyd, T. A. *Ind. Eng. Chem.* **16**, 894 (1924).

8. Callendar, H. L., and others. *Aer. Res. Comm. R. and M.* 1062 (1927); *Engin.* (4, 11, 18 Feb. 1927).
9. Campbell, C., and Woodhead, D. W. *J.C.S.* 3010 (1926).
10. Carr, M. S., and Brown, G. G. *Ind. Eng. Chem.* **21**, 1071 (1929).
11. Chapman, D. L. *Phil. Mag.* (v), **47**, 90 (1899).
12. Dumanois, P., Mondain-Monval, P., and Quanquin, B. *Compt. rend.* **192**, 1158 (1931).
13. Egerton, A. C. *Nature*, Suppl. 122, 20 (1928).
14. —— *Nature*, 120, 694 (1927).
15. Egerton, A. C., and Gates, S. F. *Aer. Res. Comm. R. and M.* 1079 (1927).
16. —— —— *Proc. Roy. Soc.* **114**, 137 and 152 (1927); **116**, 516 (1927).
17. —— —— *J.I.P.T.* **13**, 244 (1927).
18. Egerton, A. C., and Pidgeon, L. M. *Proc. Roy. Soc.* **142**, *A*, 26 (1933).
19. Egerton, A. C., Smith, F. L., and Ubbelohde, A. R. *Proc. Roy. Soc.* **234**, 433 (1935).
20. Emeleus, H. J. *J.C.S.* 2948 (1926); 1733 (1929).
21. Evans, E. B., Dodds, E., and Garner, F. H. *J.I.P.T.* **21**, 1,000 (1935).
22. Fenning, R. *Rep. and Mem. Aer. Res. Comm.* 979 (1925).
23. Fowler, A. *Proc. Roy. Soc.* **142**, *A*, 362 (1933).
24. Garner, F. H., Evans, E. B., Sprake, C. H., and Broom, W. E. J. *Proc. World Petr. Congr.* **2**, 170 (1933).
24*a*. Gill, F., Mardles, E. W. J., and Tett, H. C. *Trans. Faraday Soc.* **24**, 574 (1928).
25. Glyde, H. F. *J.I.P.T.* **16**, 756 (1930).
26. Hinshelwood, C. N., and Williamson, A. T. *The Reaction between Hydrogen and Oxygen* (Clarendon Press, Oxford, 1934).
27. Jones, L. T., and Bates, J. R. *J.A.C.S.* **56**, 2285 (1934).
28. Jost, W. *Z. f. Elektrochem.* **41**, 197 (1935).
29. Jouguet, E. *J. de Math.* 347 (1905), and 6 (1906).
30. Lenher, S. *J.A.C.S.* **53**, 2962, 3737, 3752 (1931).
31. Lewis, B. *J.A.C.S.* **52**, 3120 (1930).
32. Lewis, S. J. *J.C.S.* 1555 (1927).
33. Lewis, B., and v. Elbe, G. V. *J. Chem. Phys.* **2**, 537 (1934).
34. Lorentzen, J. *Z. Angew. Chem.* **44**, 131 (1931).
35. Lucas, H. J., Prater, A. N., and Morris, R. E. *J.A.C.S.* **57**, 723 (1935).
36. Mardles, E. W. J. *Aer. Res. Comm. R. and M.* 1374 (1930).
37. Marvin, C. F. N.A.C.A. Tech. Rep. no. 276 (1927).
38. Maxwell, G. B., and Wheeler, R. V. *J.I.P.T.* **14**, 175 (1928).
39. Midgley, T. *J.S.A.E.* **7**, 489 (1920).
40. Mondain-Monval, P., and Quanquin, B. *Ann. Chim. Phys.* **15**, 309 (1931).
41. Mondain-Monval, P., and Wellard, R. *Compt. rend.* **200**, 232 (1935).
42. Moureu, C., Dufraisse, C., and Chaux, R. *Compt. rend.* **184**, 413 (1927).
43. Neumann, M., and Aivazov, B. *Nature*, **135**, 655 (1935).
44. Neumann, M., and Serbinoff, A. *Phys. Z. Sow.* **1**, 536 (1932).
45. Newitt, D. M., and others. *Proc. Roy. Soc.* **134**, *A*, 592 (1932); and **140**, 426 (1933).
46. Norrish, R. W. *Proc. Roy. Soc.* **150**, 869 (1935).
47. Nusselt, W. *Z.V.D.I.* **59**, 872 (1915).
48. Pease, R. N. *J.A.C.S.* **51**, 1839 (1929), et seq.
49. —— *J.A.C.S.* **57**, 2296 (1935).
50. Pidgeon, L. M., and Egerton, A. C. *J.C.S.* 661 (1932).
51. Pignot, A. *Compt. rend.* **185**, 111 (1927).
52. Prettre, M. *Ann. Comb. liq.* **6**, **7**, 269, 533 (1931) et seq.
53. Rassweiler, G. M., and Withrow, L. *Ind. Eng. Chem.* **27** (1935).
54. Ricardo, H. R. *Proc. Inst. Aut. Eng.* **18**, Pt. 1 (1923).
55. Rice, F. O. *Ind. Eng. Chem.* **26**, 259 (1934).
56. Semenoff, N. *Chemical Kinetics and Chain Reactions* (Clarendon Press, Oxford, 1935).
56*a*. Sims, C. J., and Mardles, E. W. J. *Trans. Faraday Soc.* **22**, 363 (1926).
57. Smith, H. A., and Kistiakowski, G. B. *J.A.C.S.* **57**, 835 (1935).
58. Steacie, E. W. R. *Proc. Roy. Soc.* **146**, *A*, 388 (1934).
58*a*. Stevens, F. W. *J.A.C.S.* **48**, 1896 (1926).
59. Tizard, H. T. *Proc. N.E. Coast. Inst. Engrs.* (1921).
60. Tizard, H. T., and Pye. *Phil. Mag.* (6), **44**, 79 (1922); (7), **1**, 1094 (1926).
61. Thompson, H. W., and Hinshelwood, C. N. *Proc. Roy. Soc.* **125**, *A*, 277 (1929).
62. Townend, D. T. A. *Proc. Roy. Soc.* **143**, *A*, 168 (1933), et seq.
63. Ubbelohde, A. R. *Proc. Roy. Soc.* **152**, 354 (1935).
64. Ubbelohde, A. R., and Egerton, A. C. *Nature*, **135**, 67 (1935).
65. Ubbelohde, A. R., Drinkwater, J. W., and Egerton, A. C. *Proc. Roy. Soc.* **153**, 103 (1935).
66. Weerman, R. A. *J.I.P.T.* **13**, 300 (1927).
67. Wendlandt, R. *Z. Phys. Chem.* **116**, 227 (1925).
68. Withrow, L., and Boyd, T. A. *Ind. Eng. Chem.* **23**, 539 (1931).
69. Withrow, L., Lovell, W. G., and Boyd, T. A. *Ind. Eng. Chem.* **22**, 945 (1930).
70. Withrow, L., and Rassweiler, G. M. *Ind. Eng. Chem.* **23**, 769 (1931), **24**, 528 (1932).
71. —— —— *Ind. Eng. Chem.* **25**, 923, 1359 (1933).
72. —— —— *Auto. Eng.* **24**, 281 and 385 (1934).
73. Wawrzinick. *Automobiltechnische Z.* (Feb. and March 1932).

2. THEORY OF KNOCK IN INTERNAL-COMBUSTION ENGINES

By HAROLD A. BEATTY, Ph.D., and GRAHAM EDGAR, Ph.D.

Research Department, Ethyl Gasoline Corporation, New York

OF the various kinds of irregular or abnormal combustion which may occur in an engine, the most important from both the theoretical and practical points of view is the type variously known as knock, pink, or detonation. Knock may be defined as an abnormally rapid explosion of a certain portion of the charge which is the last to burn in an internal-combustion engine, resulting in the formation of pressure-waves in the gas. It is a characteristic of engines of the Otto-cycle type, operating under specific conditions, and is to be distinguished from other kinds of abnormal combustion, such as pre-ignition and after-firing. These latter phenomena are different in nature from knock, and accordingly will not be dealt with here, although they may be of considerable practical importance. Effects similar to those of knock are shown by Diesel engines when running 'rough', and the two phenomena are somewhat related; however, the study of the latter has been approached from a different point of view, and the results obtained have not contributed significantly to an understanding of the nature of knock. The present discussion is therefore confined to knock in engines of the Otto-cycle type.

The occurrence of knock was known as early as about 1882 [7], but detailed investigations of the phenomenon did not begin until much later. Around 1918 extensive studies of the problem were under way by Kettering [16] and his associates in the United States, and by Ricardo [26] in England. Pre-ignition and knock were clearly distinguished, and Ricardo stated that the latter resulted, not from mechanical defects in the engine, but from a simultaneous and spontaneous ignition of the last part of the charge to burn.

However, the lack of correlation between the knocking tendency and the spontaneous ignition temperatures of different fuels, together with the announcement in 1920 and 1922 by Midgley and Boyd [21] of the discovery (some years previous) of the anti-knock effect of very small amounts of different compounds, cast considerable doubt on the correctness of the simple spontaneous ignition theory. As a result, various speculations were advanced in explanation of the nature of knock and its suppression. These ideas were based upon experimental facts which, in large part, had been obtained under conditions more or less different from those found in an engine, and a considerable degree of confusion and several distinctly erroneous conclusions resulted therefrom.

Further experimentation, in recent years, conducted directly with engines or in closely related apparatus, brought out a series of facts which has done much to dispel the existing confusion and contradictions; concurrently, the development of the chain-reaction theory of the slow oxidation and explosion of gases has provided a reasonable basis for the explanation of the phenomena observed. Consequently, it is now possible to advance a general outline of the nature of engine combustion, knock and anti-knock action, which is in accord with the known facts and appears to be theoretically sound. A great many details remain to be filled in, and a number of major points are still in doubt, but certain basic facts appear to be well established.

The following survey first reviews these facts, and then considers their possible theoretical interpretation. No attempt is made to refer to the extensive literature on the subject of knock in its entirety; rather, there is presented only a selection of those data and conclusions which have been instrumental in establishing our present conception of the nature of the process.

Experimental Evidence as to the Nature of Knock

Normal Combustion. In non-knocking combustion the flame, starting from one or more points of ignition, travels through the charge with a moderately fast velocity, but shows no indication of pulsations or vibration. A detailed description of flame travel is given in articles 7, 8, and 9. In engine cylinders the flame has been recorded photographically and electrically, using windows or ionization measuring plugs located at different points in the cylinder head [15, 1930; 20, 1927-31; 28, 1932-34; 37, 1931-32; 39, 1931]. The flame speeds, relative to the cylinder-head walls, usually range from 25 to about 250 ft. per sec. in a conventional type of engine, with a maximum value at the point where some 50% of the charge has been burned. They are determined principally by the degree of turbulence in the charge, which in turn is largely a function of combustion-chamber design and engine speed. Secondary factors of more or less influence on the flame velocity are the temperature of the combustion-chamber walls; the design, location, and temperature of the sparking-plugs and valves; together with the chemical composition of the fuel, the air-fuel ratio, and the charge temperature and dilution by exhaust gas. The compression ratio, the charge density, and the spark advance have little or no effect on the actual flame speeds [31, 1927-31].

Combustion of the fuel is practically complete within the narrow flame front, yielding carbon monoxide, carbon dioxide, and water [18, 1934; 38, 1930]. The traces of hydrocarbons found in exhaust gases result from the thermal decomposition of unvaporized fuel and oil on the cylinder walls. When the gases behind the flame front begin to cool down, readjustments occur in the equilibria, $2CO+O_2 \rightleftharpoons 2CO_2$, $CO+H_2O \rightleftharpoons CO_2+H_2$, and $H_2+2OH \rightleftharpoons 2H_2O$, in the direction from left to right in each case. When, as is usually the case, the initial mixture is rich, i.e. the air-fuel ratio is less than the theoretical required for complete combustion to carbon dioxide and water, then the amount of oxygen remaining behind the flame front is very small: as a result, some of the hydrogen formed by the second of the above reactions may escape combustion and so appear in the exhaust gas.

The spectrum of the flame front in an engine is similar to that of a bunsen burner, comprising a number of well-known bands (e.g. C–H and C–C) superimposed on a background of continuous emission, the familiar blue predominating in the visible [39, 1931–2]. Unfortunately, the spectrum cannot as yet yield any detailed information as to the nature of the reactions or transformations from which it originates. Behind the blue flame appears an after-glow, whose principal visible radiation is in the yellow; its ultra-violet spectrum shows CO and OH bands; its infra-red emission indicates the presence of carbon dioxide and water, with little or no black body radiation. This afterglow does not necessarily represent a continuation of the combustion process; rather, it apparently results from the equilibrium reactions noted above, or else from the previous thermal excitation of the molecules and radicals present.

In normal combustion the pressure increases to its maximum value in a smooth, continuous manner without pulsations or vibration; the combustion proper is ordinarily entirely noiseless [36, 1933], although sound waves may be emitted if the combustion-chamber surfaces are sufficiently flexible to be able to 'diaphragm'. The rate of pressure rise depends not only on the rate of reaction and the engine speed, but also on a complexity of variables which affect the temperature, and is not constant throughout the cycle [24, 1931; 32, 1933]. Its maximum value, in modern automotive engines, is in the neighbourhood of 1,000 lb. per sq. in. per 0·001 sec.

Characteristics of Knock. The occurrence of knock in the engine is marked by flame and pressure characteristics distinctly different from those of normal combustion. These characteristics are confined to a portion of the charge, which is the last to burn; i.e. to the so-called 'end gas'. This portion of the charge which enters into knocking combustion may vary from an undetectably small amount to at least three-quarters of the whole. In any case, that portion of the combustion which precedes the knock is perfectly regular and is indistinguishable from that observed in the entire absence of knock, except that its velocity may be slightly higher (probably because of the fact that the knock increases the cylinder-head temperatures).

The flame of knocking combustion seems to sweep through the charge practically instantaneously: its actual velocity is not accurately known, but appears to be in the neighbourhood of 1,000 ft. per sec. [28, 1932–4]. This value, although much greater than the rate of normal flame travel, is definitely less than that of a true detonation wave. The latter (whose characteristics have been described in Articles 8 and 9) would have a velocity of approximately 5,000 ft. per sec. for air-fuel mixtures similar to those used in an engine, provided such mixtures could actually detonate [3, 1927]. The spectral emission of the knocking flame in general resembles that of the normal flame, but extends farther into the ultra-violet and the infra-red; the intensity is much greater than in the normal case [6, 1928; 39, 1931–2]. In addition, the C–H and C–C bands are weak or disappear in the knocking flame.

Corresponding to the high flame velocity, the rate of pressure rise resulting from knocking combustion is also high, and attains a maximum value of the order of 10,000 lb. per sq. in. per 0·001 sec. [32, 1933]. Although much higher than that occurring in normal combustion, this value is apparently less than that which would be obtained from the initiation of a true detonation wave within an engine cylinder: the latter, it has been estimated, would probably be more than the cylinder could stand [11, 1927–8]. The change from the low rate characteristic of normal operation to the high rate found when knock occurs is sufficiently abrupt and of such magnitude as to result in the formation of pressure waves [41, 1934]. These, reflected from the cylinder walls, set up a state of resonant vibration in the gas within the cylinder, while a forced vibration of equal frequency is induced in the cylinder walls, resulting in audible sound [33, 1934; 36, 1933].

Factors influencing the Tendency to Knock. Other things being equal, any change in operating conditions which tends to increase the temperature of the charge or to lengthen its time of heating prior to ignition increases the tendency to knock [34, 1934]. As might be expected, this applies particularly to the end gas, where the knock actually originates. Conversely, such factors as low temperatures of the induction system, the cylinder walls and the pistons, freedom from carbon deposits, cool exhaust valves and absence of other localized hot spots, high flame speeds and low flame temperatures, low compression ratio, high engine speeds and turbulence, suitably located sparking-plugs and the absence of pockets or dead spaces in the cylinder head, all contribute to diminish the tendency to knock. The effect of engine speed is of paramount importance; indeed, there is some indication that at very high speeds knock can never develop, although pre-ignition may set in. The influence of an increase in compression ratio is particularly marked in increasing the tendency to knock, and is due principally to its effect of decreasing the proportion of residual exhaust gas in the mixture. Usually, the presence of exhaust gas gives considerably lower flame temperatures (despite its effect of increasing the initial temperature of the charge) owing to its diluent action and high specific heat. A secondary effect of increasing compression ratio is that of increasing the temperature obtained by adiabatic compression.

All such physical or mechanical variables which are found to affect the knock may be interpreted as modifying the *temperature* or the *time* factor, or both [34, 1934]. It is not certain what effect would be given by a change in pressure, all other factors being the same, since this factor is not susceptible to completely independent variation. However, it appears that the effect, as regards flame speeds, is slight [20, 1927–31]; cf. also Article 5.

The relative effects of the time and temperature factors are not necessarily identical for different fuels. Thus, two fuels which have the same tendency to knock under one set of engine conditions may differ considerably in their relative knocking tendency when some engine variable (for example, engine speed or inlet temperature) affecting time or temperature is altered (cf. Article 15).

The tendency to knock depends not only on the physical factors of time and temperature, but also on the chemical composition of the charge. Here the significant variables are the chemical nature, concentration, and heat of vaporization and combustion of the fuel, the air-fuel ratio, the presence of compounds which act as pro- or anti-knock agents, and the degree of charge dilution by residual exhaust gas in the cylinder. In general, a chemical composition which would be expected to develop low-temperature or slow-oxidation reactions under conditions which exist in the end gas, at a relatively rapid rate and with a high temperature coefficient, increases the likelihood of knock. Evidence for the presence of such reactions is given below.

The chemical nature of the charge not only influences oxidation reactions in the end gas, but also affects to a certain degree the temperature and speed of the normal flame wave. However, there is no evidence that the flame characteristics of the charge have any relation to the tendency to knock (except indirectly, in so far as they affect the end gas). As previously stated, the normal flame which appears prior to knock is practically indistinguishable from that which appears when knock is absent. Moreover, the knocking flame seems to have the same characteristics regardless of whether knock is induced by a change in chemical composition of the charge or by a change in the physical factors of time and temperature. In brief, it appears that the chemical factors influence the *initiation* rather than the *propagation* of the knocking flame. This point will be further considered in the discussion of the theory of the process.

From the practical point of view, the most important chemical variable (apart from the action of anti-knock agents) is the chemical structure of the different compounds of which the fuel is composed, variations in which permit an extremely wide range of knocking tendency. This point is considered in detail in Article 10: in summary, it may be stated here that a certain degree of concordance between structure and anti-knock value is observed, but the relationship is by no means simple or direct and its source is not known specifically. Not only do different fuels vary greatly in their tendencies to knock, but the relative ratings of different fuels may also vary considerably with the engine conditions employed, as shown in Article 15. Generally, it appears that the oxidizability of the fuel is the basic factor in determining its knocking tendency, but no definite correlation is evident. For example, the so-called spontaneous ignition temperatures of different compounds, determined by the usual crucible or tube methods, serve only as a rough index of knocking tendency, while the temperature of initial oxidation gives an even poorer correlation.

Pro- and Anti-knock Agents. The presence of pro- and anti-knock agents is a conspicuous factor in determining the tendency to knock, and their discovery has done much to stimulate study of the mechanism of knock. Unfortunately, the actual operation of pro- and anti-knock compounds within an engine is for the most part not open to direct observation, so that the evidence as to their mode of action is largely indirect or inferential, and widely different conclusions have been drawn from the results obtained. As reported by various investigators, the significant experimental facts are, briefly, as follows.

Pro- or anti-knock effects are shown by a diversity of compounds, present in the fuel in moderate or very small concentrations (1–0·001%). The majority of the known pro-knock compounds contain chemically active oxygen or else react readily with air to yield it, and include such compounds as ozone, organic and hydrogen peroxides, nitric oxide and organic nitrites, bromine, hydrobromic acid, hydrogen sulphide, ethyl ether, aliphatic aldehydes (other than formaldehyde), &c. Probably the most effective of these are ozone and ethyl peroxide, of which as little as 0·001% in the intake air is sufficient to exert a pronounced pro-knock action [4, 1933; 13, 1934].

The anti-knock agents are discussed in Article 11; they are, in general, of the same type as the inhibitors for low-temperature, liquid-phase oxidations. The best-known agents are organo-metallic compounds and a series of aniline derivatives. On a molecular basis, the former are of the order of 100 times as effective as the latter, the distinction being so marked as to suggest a fundamental difference in their respective modes of action. As an example of the extraordinary performance of these compounds, it can be shown that as little as 1 molecule of tetraethyl lead in over 200,000 molecules of hydrocarbon is sufficient to give a noticeable decrease in knock. Both the relative and the absolute effectiveness of an anti-knock agent (e.g. the 'lead sensitivity') may vary considerably for different fuels and for different operating conditions, and for a given fuel is not necessarily proportional to the amount added.

In the case of organo-metallic compounds, it is stated by Egerton [11, 1927–8] that the molecule must be dissociated before the metal atom can be effective; correspondingly, metals in the form of compounds which are chemically stable under the conditions existing in an engine are inactive as anti-knock agents. Olin and Jebens [23, 1929] were unable to show an anti-knock effect of colloidal iron, nickel, and lead, perhaps because of the conditions of the experiments, whereas Egerton [10, 1927], using laboratory methods, found the ignition temperature of gasoline to be raised by a number of different metals in the vapour state (cf. ref. Sims and Mardles, Article 1).

Atomic lead and lead oxide bands appear in the flame spectrum of an engine using leaded fuel [39, 1931–2]; otherwise, no significant difference has been found between the normal flame which precedes knock and the same flame after addition of enough lead to eliminate the knock, except that the flame velocity may be slightly higher in the former case [37, 1931]. Likewise, the knocking flame has the same characteristics in the presence of lead (in an amount insufficient to eliminate the knock completely) as in its absence, although the amount of knocking combustion is reduced. It has also been shown that the onset of the true detonation wave in certain pentane-air mixtures contained in a long tube is unaffected by tetraethyl lead [9, 1927]. Thus, on the whole, the evidence suggests that the influence of anti-knock agents, like that of the chemical composition of the fuel, is concerned with the initiation rather than the propagation of the knocking flame; and, furthermore, that this influence is not connected with any significant alteration in the character of the normal flame travel.

Significance of Laboratory Experiments Related to Knock. Much of the experimental evidence adduced to explain the mechanism of knock and the action of anti-knock agents has been obtained in the laboratory under conditions more or less different from those which hold in the engine. This is particularly true with respect to oxidation reactions. The general subject of slow oxidation is reviewed in detail in Articles 1, 3, and 4; here it is necessary only to consider to what extent the experimental evidence is applicable to the problem of knock.

Outside of engines, practically no study has been made of the oxidation of fuel vapours, employing reaction times comparable with those which are available for the end gas in the engine, that is, of the order of 0·001–0·010 sec. Laboratory experiments on oxidation customarily involve time elements some 1,000-fold greater than these values. Furthermore, oxidation reactions in general usually exhibit an 'induction period', that is, an initial time period during which the characteristics of the reaction are markedly different from those which subsequently appear. This induction period may be so short as to be overlooked in laboratory experiments, yet the reactions involved therein may well be the factors of prime importance in an engine.

The conditions of temperature, likewise, are often notably different in laboratory and engine studies. In the former case, operation at 500° C. or below is necessary to avoid ignition or explosions whose occurrence, after a brief delay period, makes the examination of the preceding reactions practically impossible; the majority of work on oxidation and ignition has been carried out in the neighbourhood of 300° C. In the engine, the maximum temperature attained by the end gas, just before its inflammation, can only be roughly estimated, but it is probably above 500° C. in most cases. Thus, as a first approximation, we may assume that that part of the charge which is the last to burn undergoes adiabatic compression from 1 to a maximum of 40 atm. by virtue of the movement of the piston and the combustion of the rest of the charge: then, with $\gamma = 1{\cdot}33$, and an initial temperature of 100° C., the final calculated temperature is 660° C.; for a compression to only 10 atm., the corresponding final temperature is 390° C. If anything, these calculated temperatures are probably too low, since the heat gained by the end gas, from chemical reaction and absorption of radiation from the advancing flame front, is most likely greater than that lost to the cylinder walls.

In addition, engine operation involves two factors—the turbulence of the charge and the effect of the combustion-chamber surfaces—which are not duplicated in other types of apparatus. The influence of these factors on the preflame reactions in the end gas is unknown, but may well be considerable, especially for the former of the two.

On the whole it follows that correlation between laboratory experiments on oxidation and engine performance is not necessarily to be expected and should be attempted only with caution; evidence obtained in this manner as to the nature of events in an engine cannot be considered as more than tentative.

Preflame Reactions in the Engine. Fortunately, a certain amount of reliable knowledge concerning the preflame reactions has been obtained directly from engines in actual operation, principally from the investigations of Boyd, Rassweiler, Withrow, and associates. The facts obtained are most significant. In non-knocking operation no indication is found of any extensive chemical change in the end gas. When the fuel or operating conditions are changed in the direction to produce knock, absorption spectra show the presence of formaldehyde in the non-inflamed end gas, in amounts which increase as the threshold of knock is approached [25, 1933–5]. Concurrently, the flame spectra show a decrease in the emission of C–C and C–H bands, suggesting that the original fuel molecules have been partially oxidized or dissociated before the arrival of the flame front [39, 1931–2].

In knocking combustion, absorption spectra of the end gas begin to show the presence of formaldehyde about 0·001 sec. before the knock in an engine running at 600 r.p.m. [25, 1933–5]; other unidentified products giving a continuous absorption spectrum are also present [40, 1933]. The concentration of formaldehyde increases up to the point of inflammation; it is independent of the intensity of knock, but varies with different fuels of equal knock intensity. Suppression of the knock by a change in operating conditions eliminates the formaldehyde, as does the addition of the anti-knock agent, aniline. When tetra-ethyl lead is used, it is stated that this effect does not occur; however, the presence of lead does reduce the continuous absorption referred to above. At the same time atomic lead lines appear in the spectrum, but no lead monoxide lines have been detected, although separate experiments indicate that the latter are stronger than the former in the absence of fuel vapour.

It has also been found possible to obtain a direct, though incomplete, chemical analysis of the end gas. Samples taken from the end zone of an engine actually running, or motored over (while still hot) without ignition, show the presence of aldehydes and substances of the peroxide type when operating under knocking conditions [12, 1933; 19, 1928; 22, 1931]. In non-knocking operation no peroxides are detected; aldehydes may or may not be found.

Adiabatic compression of an inflammable mixture results in spontaneous ignition after a certain time interval, provided the temperature attained at the end of the compression stroke is so high that the subsequent heat loss to the cylinder walls is less than the heat evolution from preflame oxidation. The relation between the time lag before ignition and the compression temperature is found by Tizard and Pye [35, 1922, 1926] to conform to a simple logarithmic function, obtained by assuming that the rate of heat loss is constant, while that of heat evolution follows an Arrhenius temperature coefficient equation. These authors' results covered a range of time lags of approximately 0·05 to 0·6 sec., for which the minimum compression temperature necessary for the ignition of a heptane-air mixture was (in the particular apparatus used) from 325 to 280° C. Extrapolation of their equation to a time lag of only about 0·001 sec. is quantitatively meaningless, since the slightest change in the selected temperature-coefficient constant would have an enormous effect on the calculated ignition temperature at that short time lag; moreover, there is no assurance that the same relation between time and temperature continues to hold down to 0·001 sec. Nevertheless, it appears that the ignition temperatures for such short time lags are probably no lower than indicated by an equation of the type given by Tizard and Pye, and from their equation it can be estimated that the spontaneous ignition of heptane-air in 0·001 sec. requires a temperature of roughly 500° C. A series of different fuels may have widely different temperature coefficients, with the result that the relative ease of ignition at low temperatures and long time lags may not be in the same order as that found in an engine. For example, carbon disulphide under ordinary conditions has a very low ignition temperature, but its temperature coefficient is also low, so that for a very short time lag the required temperature is much higher than that for *n*-heptane: in accord with this, the former compound has the lesser knocking tendency. The occurrence of spontaneous ignition in the engine, starting from some point in the end gas remote from the advancing flame front, has not been positively established, but there are very clear indications of its reality in some of the photographs of engine flames [8, 1932; 37, 1931]. There is some evidence that the ignition may originate from only one or a few closely related centres of activity in the compressed gas; on the other hand, there is no particular experimental reason for believing that the entire mass of gas ignites 'simultaneously' other than to account for the high apparent flame velocity.

The effect of anti-knock agents on spontaneous ignition temperatures, determined by tube or crucible methods, has been extensively investigated. However, as previously indicated, it is very doubtful to what extent the results so obtained may be applied to ignition by adiabatic compression, in view of the great difference in the time and temperature factors involved.

Theory of the Cause and Suppression of Knock

Having listed above the principal facts known at present with respect to knock and anti-knock action, there remains the question of whether these facts can be fitted into a reasonable and consistent mechanism which will provide at least a partial explanation of the phenomena observed. In so doing, a certain degree of confusion may be avoided by considering first the nature of knock itself, and deferring until later the problem of the action of anti-knock agents. In approaching the subject of knocking combustion it is desirable to make a preliminary study both of the characteristics of true detonation waves and of the probable mechanism of normal flame travel.

The True Detonation Wave. At the outset it may be assumed that knock results either from a special type of inflammation or else an actual detonation of a portion of the charge, or from a combination of the two. The term 'detonation' here is reserved to define that specific and distinctive type of combustion in which the flame front moves with the maximum velocity which the combustible mixture is chemically capable of maintaining. The nature of detonation is fully discussed in Articles 8 and 9; here it is only necessary to recall that the ability of a given mixture to maintain a detonation wave, the minimum energy required to initiate the detonation, and the characteristics of the subsequent wave are intrinsic physical constants of the mixture, determined almost wholly by its chemical composition alone, and independent of the means by which the phenomenon is brought about. The wave is propagated, according to Lewis [17, 1930], by a series of so-called chain reactions in which the hot, energy-rich reaction products are projected from the flame front into the adjacent layer of cold, unburned gas, and furnish the latter with sufficient energy of activation for it to react. The term 'chain reaction' designates in general any self-propagated chemical reaction in which the energy evolved is not immediately diffused throughout the system, but is, at least in part, transferred directly to reactant molecules in such manner and amount as to provide the necessary energy of activation for them to react. The mechanism of this transfer may be either physical or chemical. In either case, the reaction of a single molecule, brought about by thermal excitation or any other means, serves as the starting-point of a sequence or chain of successive reactions: these processes are termed, respectively, the initiation and the propagation of the chain, and the reaction products or 'hot molecules' which transfer the energy between each step are known as chain carriers. These single chains are not infinitely long, but are eventually interrupted or broken by the deactivation of a chain carrier in such a manner (e.g. at a wall surface) that no further reaction results. Then, all other things being equal, a condition is quickly established in which the number of chains initiated and broken in unit time is equal, and the velocity of the reaction is constant, being the product of the number of chains started and their average length. However, in many cases the heat of reaction is so great that occasionally one single reaction brings about two new ones instead of only one: that is, the chain has branched. If the conditions of the system change with time in such a manner as to increase the probability of this chain-branching, then finally, at a certain critical point, the over-all probability of the chain extension becomes just greater than unity: that is, the chains not only *extend* in space, but also *multiply* themselves in a geometric progression. This branched-chain process is characterized by the very brief time interval which it may require to accelerate from an inappreciable to an explosive velocity. This concept of chain reactions has been developed by several investigators and is discussed in detail by Semenoff [29, 1935]. It has provided a satisfactory explanation of the mechanism of many reactions whose kinetics are entirely incompatible with the older theories of reaction velocity. On the average, for every reaction-product molecule that is deactivated in this process at least one new energy carrier is formed, so that a continuous chain of energy transmission is established. In the case of the detonation wave it is supposed that the energy of the chain carriers is so great that very nearly each collision with a reactant molecule leads to an immediate activation and reaction of the latter. Consequently, the reaction velocity is determined solely by the speed with which the chain carriers move: owing to their high temperature, velocities of over 10,000 ft. per sec. are obtained for fast-burning mixtures. Thus the flame of chemical combustion and the accompanying pressure wave sweep through the charge simultaneously, with identical velocities. This simultaneity is the distinctive and unique characteristic of true detonation, as compared with all other types of combustion. Because the term 'detonation' has this specific and long-established meaning, it is perhaps unfortunate that it was ever applied to the phenomenon of knock, whose nature was not definitely known. This is now particularly so since the majority of present-day students of the subject are agreed that true detonation seldom, if ever, occurs in knocking combustion. It cannot be stated categorically that a typical air-fuel mixture in an engine is incapable, in the time available, of furnishing the energy necessary to initiate detonation in the remainder of the mixture, for the reason that the question has never been put to experimental proof and cannot yet be solved on a purely theoretical basis. Nevertheless, the available evidence, summarized by Egerton [11, 1927–8] and Bone and Townend [3, 1927], indicates that it is very unlikely that detonation can occur in an engine operating in the usual manner on customary types of air-fuel mixtures. The experimental data presented earlier in this article, particularly the actual flame velocity in knocking combustion observed by Schnauffer [28, 1932–4], support this view. In a recent summary, Boerlage and Van Dyck [2, 1934] distinguish between knock and detonation, but hold that the latter may actually occur in an engine: their evidence for this is not convincing, as pointed out by Fraser [14, 1934].

The Normal Flame Wave. Although true detonation may never occur in an engine, there is no *a priori* reason why there should not exist types of inflammation other than that exhibited in the normal flame wave, which may be intermediate in character between the normal flame and the detonation wave. At the present time, theoretical considerations alone are unable to give any positive information on this question, largely because the nature of the normal flame wave itself, i.e. of slow inflammation in general, is not well understood. In particular, it is not at all clear why an ordinary flame moves as slowly as it does, especially in mixtures in which it is known that a detonation wave could be maintained if sufficient energy were provided to start it. The classic theory holds that the velocity of slow flame propagation is determined by the rate at which heat conduction from the flame front raises the adjoining layer of unburned gas to its 'ignition temperature'. In the light of modern chemistry this conception is inadequate, as Lewis and Von Elbe [18, 1934] remark, since it omits all consideration of the role played by the active atoms and radicals known to exist in the flame front. The presence of active atoms and radicals in the flame front suggests at once the application of the chain-reaction theory to the problem of the normal flame, since such atoms and radicals are a frequent factor in the propagation of reaction chains.

We have already seen that the concept of chain reactions provides a satisfactory explanation of the detonation wave. It is known, also, to govern the kinetics of slow autoxidation and the accompanying chemiluminescence of hydrocarbons (cf. Articles 3 and 4). It seems, therefore, very probable that ordinary hydrocarbon flames involve these chain reactions. In this case, to account for the relatively slow velocities observed, it is only necessary to assume that the chain carriers undergo a considerable number of fruitless collisions with the reactant molecules between each succeeding step in the reaction. That is, the interaction between the chain carrier and the reactant molecule does not appear as a simple physical transfer of energy, but partakes of the nature of a chemical reaction and itself requires an energy of activation. There is abundant evidence for the existence of chain reactions of this kind in many gas-phase reactions of the elementary type whose kinetics have been studied, and there seems no reason why such reactions should not occur in hydrocarbon flames as well.

On this hypothesis, the flame velocity is a function of such variables as the number of chain carriers emitted, their available energy, and the surplus energy of activation which the reactant molecule requires for its interaction with the chain carrier. These quantities, in turn, are dependent, in order of increasing importance, on the pressure, temperature, and chemical composition of the unburned gas. If these variables remain constant (as in the case of a gas mixture fired in an open tube in which there are no reflected pressure waves), then the flame velocity should be a constant for each particular case: this is found experimentally to be so, as shown in Article 8. In the extreme case, if the efficiency of chain transmission is very low or the surplus energy of activation required is high, then the heat of reaction does not remain concentrated in the chain carriers, but becomes, at last, diffused throughout the unburned gas; the flame then travels on the crest of a heat wave, i.e. by the classical mechanism. On the other hand, under favourable conditions the flame may be expected to travel with a velocity much greater than that determined by the simple conduction of heat, but still less than that of the detonation wave.

In an engine, the pressure, temperature, and chemical composition of the unburned gas ahead of the flame front are continuously changing, and the flame velocity might be expected to show a regular increase as the combustion proceeds. Actually, the rate of flame travel, relative to the cylinder-head walls, usually reaches a maximum at or before the mid-point of the combustion, and then declines more or less until either the charge is fully burned or knock occurs [20, 1927–31; 28, 1932–4; 37, 1931]. The maximum velocity is, however, much greater than that which would be obtained under conditions which were the same, except for the absence of turbulence and mass movement in the charge. The result of decreased turbulence, after the flame passes the centre of the combustion zone, may be so marked as completely to obscure the effect of those changes in the unburned gas which tend to increase the flame rate.

Accordingly, the normal flame in an engine may be considered in general terms as a series of chemical reactions whose progress is self-inhibited until a condition of dynamic balance is attained; at this point the intrinsic rate is determined principally by the chemical make-up of the charge, while the much greater visible velocity is established by turbulence.

The Flame Wave of Knock. The question then arises, by what mechanism or under what conditions may a flame be propagated with velocity characteristics intermediate between those of normal flame travel and of detonation? In this connexion it is pointless to distinguish between a flame originating at one single spot and spreading with abnormal rapidity throughout the gas, and a 'simultaneous' or spontaneous ignition developing from a large number of separate foci at nearly the same instant. In both cases the initial condition of the charge is presumably about the same—a state of extra-inflammability, with very little energy of activation required to bring about reaction—and the final conditions—the state of complete combustion—are essentially identical, so that in a thermodynamic sense the two modes of inflammation are the same. In any event there no longer exists in either case that condition which restricted the velocity of the normal flame to its low value.

A review of the experimental facts in the first part of this article indicates clearly that the nature of this change in the unburned charge consists in an alteration of the chemical composition thereof, produced by the development of slow oxidation reactions. Profound variations in temperature and pressure alone, without accompanying chemical change, have no noticeable effect on the inflammability, whereas in every case in which extensive oxidation occurs in the end gas there results a knock or a state of incipient knock.

It is evident that in any brief interval of time the total change in the chemical composition of the end gas produced by its slow oxidation will be very slight. Hence it may at first glance appear strange and unlikely that such a relatively minute change can so suddenly modify the inflammability of the gas that there occurs an abrupt transition from the normal rate of burning to knocking combustion. However, these sudden variations in rate resulting from slight chemical changes in the system are characteristic of chain-reaction processes, and are, indeed, no more extraordinary than some of the similar effects resulting from slight changes in pressure or temperature, at a critical point.

It is true that spontaneous ignition is usually regarded as the result of a local increase in temperature, without consideration of any change in chemical composition, a conception which doubtless is derived from the fact that temperature is a variable which can readily be measured, whereas slight changes in chemical composition prior to ignition are difficult to detect. Actually, the adiabatic compression experiments indicate that the final, critical increment in temperature is that derived from preceding chemical change rather than from the compression alone; in particular, one experiment of Tizard and Pye [35, 1922–6] in which two compression strokes occurred before ignition, with the second at a lower temperature than the first, strongly suggests that the chemical change in the gas during the compression, as well as its temperature, is an essential factor in determining the ignition point. It has been observed [1, 1934] that the 'upper' spontaneous ignition of a preheated hydrocarbon-air mixture flowing slowly through a glass tube of uniform temperature (near 500° C.) begins, not at the entrance of the tube, but at a point some 6 in. removed, after a contact time of about 7 sec.: during this interval no appreciable rise in temperature occurs in the gas stream, and it can only be supposed that the ignition is a result of changes in chemical composition of the mixture. While the application of these particular results to combustion in an engine is, as previously pointed out, questionable, nevertheless the sum total of the evidence is such that we may safely consider the onset of knock to be a result of chemical changes in the end gas, rather than a simple effect of temperature *per se*.

Preflame Oxidation. Since the actual mechanism of the process is still entirely obscure, it is difficult to make any suggestion as to the exact nature of the preflame reactions which induce knock, and as to how these reactions act to lower the energy of activation required for inflammation. Generally speaking, it seems probable that the original fuel molecules are partially oxidized, giving active or energy-rich products. These may subsequently, on a favourable collision with other reactants, bring about further oxidation and the formation of additional active products, thus continuing a reaction chain. On the other hand, an unfavourable type of collision will cause a deactivation of these chain carriers and a termination of the chain, the energy of the carriers being distributed throughout the gas in the form of heat. So long as this deactivation process predominates, the net effect over a given interval of time is merely a partial oxidation of a portion of the original fuel and a slow rise in the temperature of the mixture; the deactivated products are too stable or else their concentration is too small to modify the inflammability of the mixture as a whole to any considerable extent. In the absence of knock, this condition prevails in the end gas until the arrival of the flame front and the subsequent inflammation of the gas at about the normal rate.

When, however, the time and temperature factors are such that knock can occur, the kinetics of the reactions in the end gas are modified in the following way. As the temperature rises, the number of active molecules formed in unit time by spontaneous oxidation of the fuel may increase somewhat and the probability of their deactivation almost certainly becomes less. The latter is the important factor, since it increases the extension of the reaction chains and the autocatalytic production of the active products, and leads finally to the development of branching chains (cf. the footnote above). Then, at the critical point at which the probability of chain branching becomes unity, there is a sudden and very considerable increase in the concentration of activated oxidation products in the end gas. Until deactivation of these products occurs, the resulting mixture is far more inflammable than the original air-fuel mixture. Accordingly, its combustion may be abruptly completed by a flame which spreads, from one or more points, at a rate much greater than in normal inflammation.

It is evident that this process of sudden partial oxidation, followed by inflammation, does not necessarily correspond in velocity to a true detonation wave. The branching-chain reaction which forms the partial oxidation products may be extremely rapid relative to the preceding straight-chain reaction, and still have a molecular collision efficiency less than that occurring in a detonation wave. This is to be expected if, as seems quite probable, the chains are long and the coefficient of branching is low. In this event, the subsequent inflammation and complete combustion of the products from this branching-chain reaction cannot occur with the same velocity as the corresponding process in a detonation wave, since the necessary energy of activation is not provided at the same rate.

It may be noted here that the primary reaction which precedes the ignition of the end gas has been considered by some workers to be a thermal decomposition of the fuel, followed by oxidation of the resulting radicals or smaller molecules, rather than a direct oxidation of the original fuel. Thus Rice [27, 1934] has found a relation between the knock ratings of the nine isomeric heptanes and the number of hydrocarbon molecules produced from each by thermal decomposition, while Boerlage and Van Dyck [2, 1934] have correlated the cetene numbers (tendency to ignite in a Diesel engine) of different fuels with their velocities of cracking. Steele [30, 1933] supposes that free hydrogen liberated as a result of cracking is instrumental in causing knock. In general, there is no doubt that thermal decomposition and oxidation are closely related reactions, and the latter may well be more or less dependent on the former, at least in the initial stages: on this point the evidence is still inconclusive. It is certain that oxygenated products are present in considerable concentration at some stage in these preflame reactions. Regardless of whether such compounds are formed directly or as a result of a previous thermal decomposition, it appears likely that they, rather than the unoxidized products of cracking, are responsible for the development of that critical reaction velocity which results in the spontaneous ignition or abnormally rapid inflammation of the charge. However, either type of reaction—oxidation or decomposition—or the combination of both is embraced in the general theory of the process developed above, if it is assumed that chain reactions are involved in any case.

It is evident that this dependence of knock on preflame oxidation reactions provides a ready explanation for the considerable variation in knocking tendency shown by different fuels whose inflammabilities, heats of combustion, and physical properties in general are quite similar, but whose chemical reactivities show certain significant differences. The difference in effect of engine variables on the knocking tendency of different fuels is also readily explained, since it cannot be expected that a given variation in the temperature or time factors should affect the preflame reactions in the end gas identically for fuels of unlike chemical composition. Despite extensive investigations on the subject, the relation between the molecular structure of the fuel and its oxidation characteristics is still far from clear, but the results obtained to date are adequate to show that the variations in these characteristics are sufficient to account for the differences in absolute and relative knocking tendency observed.

Hence, in brief, the normal flame wave is considered to be maintained by the emission of highly energized combustion products into a relatively unreactive or stable gas, whose subsequent reaction is, accordingly, moderately slow; in knocking combustion, the flame passes through a mixture which, just previously, has become charged with reactive products of partial oxidation, in a concentration sufficient to permit a relatively rapid flame development or travel.

The foregoing hypothesis as to the manner in which the normal flame travels and the knock is initiated is admittedly speculative, and must be so since there is little or no direct experimental evidence as to the actual mechanism involved. It is in general agreement, in so far as the origin of knock is concerned, with the conclusions of most of the other investigators who have considered the subject in a comprehensive manner. Thus Egerton [11, 1927–8] considers that slow oxidation in the end gas by a chain-reaction mechanism leads to the formation of molecules in high energy states, which then undergo a rapid, enhanced combustion; Mondain-Monval and Quanquin [22, 1931] suggest that the fuel is broken up into oxygenated fragments which, when formed in sufficient quantity, permit an abnormally rapid rate of combustion by virtue of their high latent energy.

In modification of the spontaneous ignition theory, Callendar [5, 1927] has claimed that 'peroxide' substances are formed in nuclear drops of unvaporized fuel and there act as ignition primers, so that these fuel drops become foci for the sudden ignition of the unburned charge. This hypothesis cannot be considered satisfactory since it fails, among other things, to account for knock in mixtures known to be entirely in the gaseous condition, and to explain the sensitive dependence of knock on mixture strength.

Pro- and Anti-knock Action. The theory of the mechanism of the normal and knocking flames outlined above indicates a relation between these phenomena and the chemical composition of the fuel charge, but contains no reference to the action of pro- and anti-knock compounds which may be highly effective at a concentration so small that the bulk composition of the fuel remains virtually the same as in their absence. Indeed, such a theory could have been devised quite independently of all knowledge of pro- and anti-knock action, and could still be considered valid, but actually it receives its strongest support from the fact that it embraces the only mechanism yet found satisfactory to explain the effect of anti-knock agents—that is, the inhibition of chain reactions in the end gas.

Prior to the development of the idea of chain reactions, many different mechanisms were proposed for anti-knock action, and conceptions of the nature and cause of the knock itself, which corresponded with these mechanisms, were put forth. In general, these theories are unable to account for more than one or two of the following essential facts: (1) a single molecule of an anti-knock compound can distinctly affect the knocking tendency of over 200,000 molecules of fuel; (2) the same is true of pro-knock compounds, and these two actions are mutually antagonistic; (3) these effects are chemical rather than physical properties of the compounds in question, and appear in general to be chemical rather than physical phenomena; (4) they are manifested in the brief time interval prior to the inflammation of the charge; (5) the change from normal to knocking combustion is abrupt rather than continuous.

Among the earliest theories proposed are those which ascribe to anti-knock agents a positive catalytic action whereby combustion of the fuel is promoted during the early stages of the cycle, thus avoiding a sudden release of energy in the final period. These ideas are so at variance with most of the experimental facts that they have long been abandoned. However, this conception led to the discovery of anti-knock compounds by Midgley [21, 1920–2], since it was supposed that coloured compounds in the fuel might reduce knock by absorbing radiant energy from the advancing flame front, thereby promoting the vaporization and subsequent combustion of the fuel: the first compound selected for this purpose was iodine (which happens to have considerable anti-knock value). Further experiments with oil-soluble dyes at once made it apparent that this theory was incorrect. It is still uncertain to what extent radiation from the flame front influences the preflame reactions in the end gas, but it is now clear that anti-knock agents have no significant effect on the radiation itself.

Conversely, theories of anti-catalytic surface action have been advanced, primarily based on the idea that the simplest way to account for the effectiveness of a minute amount of an anti-knock agent is to consider that it poisons or suppresses the action of a normally present surface catalyst. The anti-catalyst is regarded as concentrated at the active spots on the combustion-chamber surface where the reactions leading to knock are initiated. However, there is little evidence for the occurrence of significant surface reactions in an engine, while, on the other hand, there are many indications that pro- and anti-knock action takes place in the gas phase: consequently, theories of surface action of this type have been discarded.

It has also been suggested that ions projected from the flame front activate the unburned portion of the charge to a state where abnormally rapid combustion becomes possible, and that anti-knock agents absorb this electrical energy and later discharge it in such wise as to prevent activation of the fuel. While it is probably true, as pointed out above, that the emission of ions is an important method of flame propagation, it remains to be shown that these ions can do more than continue the progress of the normal flame wave in a given mixture, and an explanation of anti-knock action on this basis is inconsistent with the chemical nature of that action.

Anti-oxidant Action. All of these and other similar theories seem untenable as soon as it is clearly realized that the ignition of gases in general and knock in particular are not isolated phenomena, but are invariably accompanied by a period of preflame autoxidation, and that the anti-knock compounds are efficient inhibitors (often incorrectly termed 'negative catalysts') for such autoxidations, while pro-knock compounds have the opposite effect. The development of this conception has been retarded by the fact that, until recently, the experimental data on which it is based were obtained under conditions often radically different from those prevailing in an engine; as a result, the correlation of these data with engine performance was very uncertain, and several different interpretations of the results have been advanced. Nevertheless, the following two primary facts are evident.

First, the onset of knock is an ignition essentially similar in kind to the much slower ignitions observed in crucibles, tubes, and adiabatic-compression machines. These ignitions are invariably preceded by a time interval during which autoxidation occurs, the length of this interval being determined by the velocity of oxidation and its temperature coefficient, on the one hand, and by the inflammability of the charge on the other. Since these two factors are, at least to a certain degree, independent of each other, it follows that both must be separately considered in determining the tendency of a given fuel to knock, and in evaluating the effect of anti-knock compounds. Accordingly, it does not appear necessary to invent any mechanism whereby anti-knock agents affect the innate inflammability of the fuel, provided it can be shown that these agents do modify the velocity of preflame oxidation to an extent sufficient to account for the observed diminution of knock.

Second, the anti-knock compounds unquestionably are inhibitors of the slow oxidations which precede ignition in tubes and crucibles, and there is no reason to suppose that they do not have the same action during the shorter time of preflame reaction in an engine. It is true that the latter supposition was not until recently put to direct experimental test, but spectographic investigations of Withrow and Rassweiler [25, 1933–5; 40, 1933] have now provided a certain amount of definite evidence for the correctness of this hypothesis. Our knowledge of gas reactions in general indicates that there is no time lag or induction period in the action of an inhibitor (as is sometimes the case for a positive catalyst), provided the inhibitor is available in its reactive form. This last qualification is presumably responsible for the failure to observe the expected effect of anti-knock agents on some of the ignitions in adiabatic-compression machines.

This general conception—that pro- and anti-knock compounds alter the ignition characteristics of the unburned charge by modifying the amount or velocity of preflame oxidation therein—at once provides a valid explanation for the various different features which characterize pro- and anti-knock action, particularly the chemical nature thereof. However, the detailed development of this pro- and anti-oxidant theory has taken several different forms, owing to the different interpretations placed on the results of laboratory experiments and the lack of knowledge as to the exact conditions existing in an engine.

Chain-reaction Theory. The reactions involved in this pro- or anti-oxidant action are variously considered as peroxidations, hydroxylations, thermal or oxidative decompositions, &c., or, in more simple and general terms, as chain reactions. This last designation, although for some reason objected to by certain authors, appears at the present time definitely preferable to any other more specific definition, since it involves no assumptions whatever as to the actual reaction mechanism, but merely requires that the reaction propagate itself throughout the charge and that this propagation may be promoted by a pro-knock compound or interrupted by the action of an inhibitor.

Although this conception of the reaction may seem unsatisfyingly indefinite, the fact remains that, despite the extensive amount of work which has been done on autoxidations, we still have practically no knowledge of the actual mechanism involved or of the unstable intermediate products formed. All recent investigations indicate that those reaction products which can be isolated and, in part, identified, such as aldehydes, alcohols, peroxides, &c., are no more than the end products of the reaction chain; they are chemically too stable to play an active role in the reaction mechanism. The chain carriers and the chemically active products which are responsible for such phenomena as autocatalysis and induced oxidation appear to exist as such for no more than a fraction of a second, and are probably best described by the general designation of free radicals. When such radicals contain oxygen, they may be expected to have peroxide properties, but to describe them as 'peroxides' is unwarranted and leads to confusion between them and the relatively stable peroxides which have been isolated from the end gas.

Correspondingly, the specific method by which pro- or anti-knock compounds promote or repress the propagation of the reaction chains remains unknown, although there is considerable evidence that the process in each case is one of oxidation.

The pro-knock materials are usually of a chemical type which would be expected to initiate oxidation processes, and it appears probable that their function is merely that of starting reaction chains at a rate much greater than that which would normally result from thermal action alone. Then, if the absolute number of chains broken in unit time by deactivation of the chain carriers is not proportionately increased, it is clear that the critical point (where the chains are formed faster than they are broken) will be reached in a shorter time, thus giving the charge a greater opportunity to knock. Since we have no information as to how the reaction chains are normally broken in an engine, the foregoing hypothesis is in a large degree speculative, but it does embrace the known facts in as simple a manner as possible. If subsequently it appears that pro-knock agents alter not only the initiation, but also the extension and breaking of chains, the hypothesis may be expanded accordingly.

Anti-knock agents, as explained in detail in Article 11, fall into two distinct classes: metallic elements and non-metallic organic compounds. There may also be considered in this connexion the non-knocking fuels, since there is perhaps some indication that these fuels are not merely inert diluents, but may exert a slight, specific anti-knock action when blended with knocking fuels.

As a class, the metallic anti-knock agents and the organic compounds exhibit a difference in relative effectiveness so marked as to suggest a fundamental distinction between their respective modes of action. Egerton [11, 1927–8] attributes the anti-knock effect of the metallic agents to the fact that the metals in question are capable of forming two or more oxides in equilibrium at the temperature of the end gas in an engine, and that the oxide is the active agent which breaks the reaction chains. Other evidence suggests that the free metal atom is involved. In any case, it appears possible that in this process the inhibitor is not permanently destroyed or removed from the sphere of reaction, but instead is able to reform the active oxide or atom, so that each inhibitor molecule may act over and over again, in a manner analogous to that of a positive catalyst (such as an oxygen carrier) in homogeneous solution. On the other hand, the relatively unstable organic anti-knock compounds probably cannot undergo such reversible reactions in an engine, at least to any great extent. Like the organic anti-oxidants in liquid-phase autoxidations, they usually are, in the act of chain-breaking, oxidized, decomposed, or otherwise rendered ineffective for further inhibitory action, as is known to be the case in liquid-phase autoxidations.

This difference in permanency of action immediately supplies an explanation for the distinction between the metallic and organic anti-knock compounds, and accordingly appears as an attractive hypothesis, although there is very little experimental evidence bearing on the matter. However, results of spectrographic investigations [25, 1933–5], showing a notable difference in the amounts of formaldehyde formed prior to inflammation in the end gas on eliminating knock by addition of tetraethyl lead or of aniline, suggest that the action of these compounds may differ in kind as well as in degree. On the whole, it is evident that further experimentation is required before a mechanism of anti-knock action can be developed more specific than that outlined above.

Summary. Much of the foregoing discussion necessarily involves physico-chemical principles which may be unfamiliar to many readers, for whose benefit the following brief summary in simple terms is appended.

Most flames and explosions fall into the category of chain reactions in which the reaction is extended from one molecule to another by direct molecular interaction rather than by general diffusion of heat, thus giving a series or chain of consecutive reactions. The continuation of such a chain is conditioned by the efficiency with which the molecular interaction occurs.

In an Otto-cycle engine the normal type of flame moves but moderately fast, since the end gas (the unburned portion of the charge ahead of the flame front) is relatively slow to react—that is, the efficiency of the chain-continuation process is low. This results from the fact that the different kinds of fuel molecules which may be present in significant amounts are all, relatively speaking, quite stable as regards inflammation. Hence the intrinsic velocity of normal combustion is not greatly affected by wide variations in fuel composition or moderate changes in pressure and temperature, or by the presence of anti-knock agents.

Before the arrival of the flame front slow oxidation occurs in the end gas by a chain-reaction mechanism. Normally, the amount of such oxidation is slight and the products formed have no important effect on the subsequent inflammation. However, when the temperature of the gas and the time available for its oxidation are sufficiently increased, the chain-continuation efficiency increases up to a critical point. At this point the chains multiply in number very rapidly, and the partial oxidation of the unburned fuel increases abruptly. The products of this oxidation are very unstable compared with the original fuel, and, being present in high concentration, can propagate a flame with high velocity. This sudden combustion starts pressure waves in the burned gases which are responsible for the sound of knock. Although very rapid, this knocking combustion does not reach the velocity of a true detonation wave, which is a phenomenon of somewhat different nature.

Anti-knock agents act as inhibitors for the slow oxidation reactions in the end gas. Their effect is to break short the reaction chains and so prevent the chain development from reaching that critical point at which its multiplication begins.

REFERENCES

1. Beatty, H. A., and Edgar, G. *J.A.C.S.* **56**, 112 (1934).
2. Boerlage, G. D., and Van Dyck, W. J. D. *J. Roy. Aero. Soc.* **38**, 953 (1934).
3. Bone, W. A., and Townend, D. T. A. *Flame and Combustion in Gases.* Longmans, Green & Co., London, 1927.
4. Brooks, D. B. *J.I.P.T.* **19**, 835 (1933).
5. Callendar, H. L. *Engineering*, **123**, 147 (1927).
6. Clark, G. L. *J.S.A.E.* **23**, 167 (1928).
7. Clerk, D. *Trans. Faraday Soc.* **22**, 338 (1926).
8. Duchêne, R. *N.A.C.A. Tech. Mem.* no. 694 (1932).
9. Egerton, A., and Gates, S. F. *Proc. Roy. Soc.* (London), *A*, **114**, 137, 152 (1927); *A*, **116**, 516 (1927).
10. — — *J.I.P.T.* **13**, 244, 256, 273 (1927).
11. — — *J.I.P.T.* **13**, 281 (1927).
   Egerton, A. C. *Nature*, **122**, 20 (1928).
12. Egerton, A., and Smith, F. Ll. *Nature*, **131**, 725 (1933).
13. Egerton, A., and Ubbelohde, A. R. *Nature*, **133**, 179 (1934).
14. Fraser, R. P. *J. Roy. Aero. Soc.* **38**, 980 (1934).
15. Glyde, H. S. *J.I.P.T.* **16**, 756 (1930).
16. Kettering, C. F. *J.S.A.E.* **4**, 263 (1919); **5**, 197 (1919).
17. Lewis, B. *J.A.C.S.* **52**, 3120 (1930).
18. Lewis, B., and von Elbe, G. *J. Phys. Chem.* **2**, 537, 659 (1934).
19. Mardles, E. *Nature*, **121**, 424 (1928).
20. Marvin, C. F., Jr. *N.A.C.A. Tech. Rep.* no. 276 (1927).
   Marvin, C. F., Jr., and Best, R. D. *N.A.C.A. Tech. Rep.* no. 399 (1931).
21. Midgley, T., Jr. *J.S.A.E.* **7**, 489 (1920).
   Midgley, T., Jr., and Boyd, T. A. *Ind. Eng. Chem.* **14**, 589, 849, 894 (1922).
22. Mondain-Monval, P., and Quanquin, B. *Ann. Chimie* (10), **15**, 418 (1931).
23. Olin, H. L., and Jebens, W. J. *Ind. Eng. Chem.* **21**, 43 (1929).
24. Pye, D. R. *The Internal Combustion Engine.* Oxford University Press, London, 1931.
25. Rassweiler, G. M., and Withrow, L. *Ind. Eng. Chem.* **25**, 1359 (1933); **27**, 872 (1935).
   Withrow, L., and Rassweiler, G. M. Ibid. **26**, 1256 (1934).
26. Ricardo, H. R. *Proc. NE. Coast Inst. Eng. and Ship.* **34**, 316 (1918); *Auto. Eng.* **11**, 51, 92, 130, 242 (1921); **12**, 265, 299, 329 (1922).
27. Rice, F. O. *Ind. Eng. Chem.* **26**, 259 (1934).
28. Schnauffer, K. *N.A.C.A. Tech. Mem.* no. 668 (1932); *J.S.A.E.* **34**, 17 (1934).
29. Semenoff, N. *Chemical Kinetics and Chain Reactions.* Oxford University Press, New York, 1935.
30. Steele, S. *Nature*, **121**, 724 (1933).
31. Stevens, F. W. *N.A.C.A. Tech. Rep.* nos. 280 (1927), 305 (1928), 337 (1930), 372 (1931).
32. Streeter, R. L., and Lichty, L. C. *Internal Combustion Engines.* McGraw-Hill Book Co., New York, 1933.
33. Taylor, C. F., Draper, C. S., Taylor, E. S., and Williams, G. L. *J.S.A.E.* **34**, 59 (1934).
34. Taylor, C. F., and Taylor, E. S. *J. Aero. Sciences*, **1**, 135 (1934).
35. Tizard, H. T., and Pye, D. R. *Phil. Mag.* (6), **44**, 79 (1922); (7), **1**, 1094 (1926).
36. Wawrziniok. *N.A.C.A. Tech. Mem.* no. 711 (1933).
37. Withrow, L., and Boyd, T. A. *Ind. Eng. Chem.* **23**, 539 (1931).
38. Withrow, L., Lovell, W. G., and Boyd, T. A. *Ind. Eng. Chem.* **22**, 945 (1930).
39. Withrow, L., and Rassweiler, G. M. *Ind. Eng. Chem.* **23**, 769 (1931).
   Rassweiler, G. M., and Withrow, L. Ibid. **24**, 528 (1932).
40. — — *Ind. Eng. Chem.* **25**, 923 (1933).
41. — — *Auto. Eng.* **24**, 281 (1934).

SLOW OXIDATION

3. PROCESSES OF SLOW OXIDATION LEADING TO IGNITION

By A. R. UBBELOHDE, B.Sc., M.A.
Dewar Fellow of the Royal Institution

I. MODES OF IGNITING AN INFLAMMABLE MIXTURE

A BRIEF review of the different processes whereby an inflammable mixture can be ignited is necessary in order to understand the bearing of processes of slow oxidation on ignition. These may be listed as follows:

1. The mixture of fuel and air or oxygen is suddenly admitted to an evacuated vessel maintained at the appropriate temperature. The initial pressure can be adjusted, and after a period of preflame lasting a few seconds, and usually accompanied by a faint luminosity, ignition takes place with a flash and sudden increase of pressure, provided the initial temperature, pressure, and concentration of the mixture are suitably chosen. This has been called the 'Pyrometer Method' by Mallard and Le Chatelier [57, 1913], and has been used by authors such as White and Price [97, 1919], Mason and Wheeler [60, 1922, 1924], Prettre and Laffitte [74, 1929], and Townend and others [93, 1933, 1934].

2. A modification of the above method is to admit the mixture cold, and heat the vessel at a steady rate. The temperature at which ignition occurs is observed manometrically. When the rate of heating is slow, very rapid reaction sets in in place of ignition at a critical temperature. The method has been used by Lewis [55, 1927, 1929], Pidgeon and Egerton [69, 1932].

3. The gases are allowed to flow through a tube maintained at a suitable temperature, which is varied till ignition occurs. The mixture is either preformed (Mallard and Le Chatelier (l.c.), Alilaire [1, 1917], Prettre [73, 1931], Mason and Wheeler [60, 1924], Dumanois and Mondain-Monval [24, 1928]) or the constituents are led in separately through concentric tubes (Dixon, Higgins, and Harwood [22, 1926], Dixon [22, 1934]). In this method a delay is again observed before the appearance of flame.

4. By mixing preheated streams of fuel and air in a large vessel continuously evacuated, the effect of the walls of the vessel has been largely eliminated (Haber and Alyea [41, 1930], Goldman [38, 1926]).

5. By heating the combustible mixture up to the ignition temperature by adiabatic compression, ignition takes place under somewhat different physical conditions. The method has been used by authors such as Tizard and Pye [92, 1922, 1926], Dumanois and Mondain-Monval [24, 1928], Pignot [70, 1926], Aubert, Pignot, and Villey [2, 1927].

6. A large number of ignition temperatures have been determined by methods where the physical and chemical conditions are not well defined (e.g. Moore [63, 1917, 1918, 1920], Egerton and Gates [28, 1927], Boord and Schaad [19, 1929]). Owing to the great influence which the nature and temperature of the surface, the concentration of the gases, and time of heating can have on ignition, the ignition temperatures so obtained are subject to much variation.

7. When an inflammable mixture is ignited by producing a high local concentration of active centres, as in the electric spark, processes of slow combustion only affect the resulting explosion if they have time to produce a chemical change in part of the charge. In the internal-combustion engine the phenomenon of knock is associated with such chemical changes in the last part of the charge to burn, and is due to a special type of ignition of a mixture presensitized by slow combustion (Withrow, Lovell, and Boyd [99, 1930], Withrow and Rassweiler [99, 1933], Rassweiler and Withrow [75, 1932], Egerton, Llewellyn Smith, and Ubbelohde [28, 1935]).

A study of the processes of slow oxidation leading to ignition is of importance in two ways. In the first place, in all the above methods the inflammable mixture is unavoidably subjected to a period of heating up, and the small quantities of combustion products formed during this interval may have notable effects on ignition (cf. Lewis [55, 1927–30], and the effect of aldehydes on the ignition of pentane, Townend [93, 1934]). This aspect of the problem will be referred to again in connexion with induction-period phenomena. A second and more important aspect of slow combustion rests on the assumption that the inconveniently rapid processes taking place during ignition are essentially of the same kind as those taking place a few degrees below the ignition temperature, where the rate is sufficiently slow to permit a detailed study. Our information on the mechanism of ignition rests almost entirely on the results of experiments on slow combustion in the neighbourhood of the ignition point.

II. METHODS OF STUDYING SLOW OXIDATION

According to the equation $C_3H_8+5O_2=3CO_2+4H_2O$, the oxidation of even a relatively simple fuel like propane must necessarily occur in stages, owing to the fact that the probability of the simultaneous collision of one molecule of propane with seven of oxygen is vanishingly small. When the intermediate compounds which are formed in oxidation are sufficiently stable, they can usually be isolated by suddenly chilling the mixture, and identified by various chemical means. The information given by chemical methods must, however, be supplemented by various physico-chemical studies, owing to the fact that intermediates of great importance for combustion may not be stable enough for isolation. In elucidating processes of slow oxidation, use has been made of the kinetics of the reaction, and of the significance of such phenomena as chemiluminescence, the induction period, wall effects, and the effect of positive and negative catalysts. The absorption spectra of certain intermediates has also been used to prove their formation during combustion. A brief review of the scope of each of these methods will be given before describing results with individual fuels:

(*a*) Chemical Methods.

Processes of slow oxidation corresponding to each of the methods of ignition described above have been studied by chemical means. Corresponding to methods 1 and 2, samples of a combustible mixture have been heated at a given temperature for a finite time, and suddenly chilled and analysed; alternatively, samples can be drawn off from a larger bulk at intervals. In order to obtain the intermediates, insufficient oxygen is usually added to oxidize the fuel completely (cf. Bone and others [10–16, 1902–32], Rideal and Brunner [77, 1928], Brunner [20, 1927–30], Mardles [58, 1931], Newitt [65–6, 1932–3]).

Corresponding to method 3 is the circulatory method of collecting intermediates, in which the combustible mixture is passed through a heated reaction chamber at various rates, and the mixture suddenly cooled at the exit. On account of the greater yields it affords, this method has been used very extensively, both in purely theoretical researches and in attempts to obtain valuable intermediates from petroleum by-products (e.g. formaldehyde from ethane, Marek and Hahn [59, 1932]). Amongst some of the researches important for the study of slow combustion may be cited: Bone and Wheeler [15, 1906], Wheeler and Blair [96, 1922], Gill, Mardles, and Tett [37, 1928], Prettre and Laffitte [74, 1929], Mondain-Monval and Quanquin [62, 1931], Ubbelohde [94, 1935, part II].

Corresponding with method 5, a valve for sampling the cylinder gases at various portions of the compression stroke in an internal-combustion engine has been developed by Lovell, Coleman, and Boyd [56*a*, 1927], and also by Egerton, Llewellyn Smith, and Ubbelohde [28, 1935]; owing to the accurate timing of the sampling, slow combustion occurring during an interval of 1/500 sec. can be investigated.

When the samples have been collected in one of these ways they have to be analysed for the various intermediates occurring in combustion. The various gases, CO, CO_2, H_2, H_2O, CH_4, &c., are analysed according to the standard methods of gas analysis. The following reagents may be used in testing for other products of combustion (cf. Egerton, Llewellyn Smith, and Ubbelohde [28, 1935], Mondain-Monval and Quanquin [62, 1931], Vorlander [94*a*, 1929], Manning, King, and Sinnatt [57*a*, 1928], Pease [68, 1934]):

Aldehydes. Schiff's reagent, made up by just decolorizing a 0·04% solution of rosaniline hydrochloride with SO_2, gives a magenta colour with most simple aldehydes. The sensitivity can be altered by varying the *pH*. Thus, if an equal volume of 10% H_2SO_4 is added, the reagent will react only with formaldehyde, and the addition of sodium acetate makes it more sensitive to higher aldehydes. For formaldehyde a 3% solution of aqueous aniline gives a cloudy precipitate, and phloroglucinol in conc. H_2SO_4 an orange-red colour. The use of Vorlander's reagent, dimethyl-dihydroresorcinol, may also be mentioned amongst many other methods for identifying aldehydes.

Oxides of Nitrogen. The Griess-Islovsky reagent is very sensitive. The reagent is freshly made by mixing equal volumes of 0·10% alpha-naphthylamine in N/100 acetic acid with 0·5% sulphanilic acid in N/100 acetic acid, and adding 1 c.c. glacial acetic acid for each 20 c.c. mixture.

Organic Peroxides. 0·5% potassium iodide in dilute H_2SO_4 + starch is a very sensitive reagent, but unless a suitable catalyst is used this may fail to detect certain organic peroxides. For dialkyl peroxides R–O–O–R, a trace of ferrous salt is used, and for hydro-peroxides R–O–O–H, one drop of 20% ammonium molybdate in an atmosphere of CO_2. In some cases ammoniacal lead hydroxide may be used; this gives a brown colour, and if followed by a little tetra base (tetramethyl-diamino-diphenylmethane) a clear evanescent blue is observed on adding glacial acetic acid. A less discriminating but also very sensitive test is a solution containing NH_4CNS + a completely reduced ferrous salt (Yule and Wilson [101, 1931]), which gives a blood-red colour with peroxides (cf. Egerton, Smith and Ubbelohde [28, 1935]). Titanous chloride or sulphate is also used in the detection of certain peroxides.

Olefines. Apart from their action on bromine water, these may be partly discriminated by their differing absorption by various concentrations of SO_3 in water (Manning, King, and Sinnatt [57*a*, 1928], Pease [68, 1934]).

Ethylene Oxide is detected by the use of manganous chloride (Lenher [54, 1931]).

The above reagents have also been used in a method of estimating the concentration of these substances in a stream of gas (Egerton, Llewellyn Smith, and Ubbelohde, l.c.).

Other products of importance, such as alcohols and organic acids, have to be isolated in considerably greater quantities before they can be identified from suitable derivatives (e.g. 3.5.dinitrobenzoic acid for alcohols, and the Ba salt for acids, Berl and Winnacker [5, 1928]).

(*b*) Kinetics of the Reaction.

Only the principal results of this aspect of the problem will be summarized here (cf. Semenoff, *Chemical Kinetics and Chain Reactions*, Oxford University Press). The rate of progress of a combustion reaction can usually be calculated from the rate of pressure change, since in most cases there is an increase in pressure (e.g. Hinshelwood and others [91,

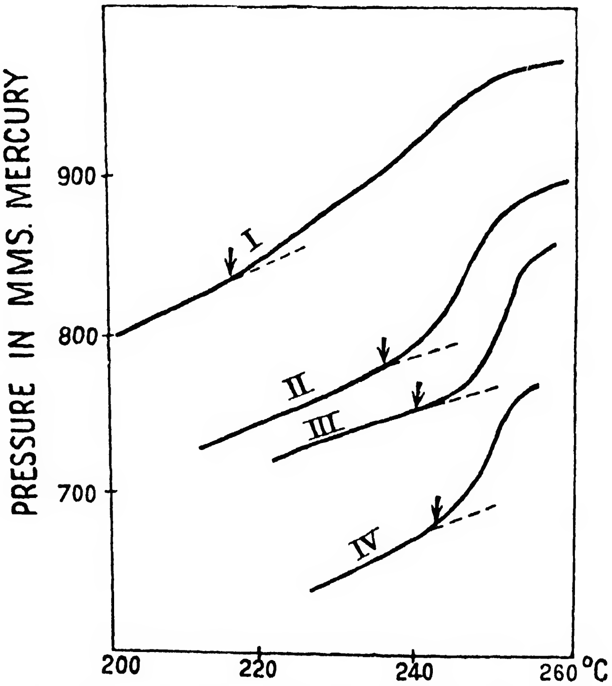


Fig. 1. Reacting temperatures (Pidgeon and Egerton). The mixture is heated to give a temperature rise of 0·6° per min. and when the mixture reacts the pressure rises abnormally.

Mixture I. Pentane : Oxygen 1 : 1 + 10% valeraldehyde.
" II. " " + 13% hexane.
" III. " " alone.
" IV. " " + 10% amylene.

1929], [31, 1930]). When the temperature of the mixture is raised at a uniform rate, instead of being kept constant (Lewis [55], Pidgeon and Egerton [69]), this increase in pressure is superposed on the steady rise. Owing to the fact that certain organic reactions such as $RCH_3+O_2=RCHO+H_2O$ can take place without pressure change, a more reliable method of following combustion is to analyse the mixture for the rate of oxygen consumption. This has been applied to the flow method in a number of cases, e.g. Edgar and others [72, 1929; 4, 1934]. From experiments on the rate of reaction, information is sought on the dependence of rate on the ratio of fuel to oxygen, on the total pressure, the temperature, and on wall effects.

In general it is found that

(*a*) Practically all combustion reactions are chain controlled, the chain length depending in a complicated way on a number of factors.

(*b*) Increasing the concentration of fuel usually has a much more marked effect on the rate, over wide regions of concentration, than increasing the concentration of oxygen, so that the propagation of the chains seems to depend on the collision of a chain carrier with a fuel molecule rather than an oxygen molecule.

(*c*) There is evidence that the chains are initiated at the walls (cf. Haber and Alyea [41, 1930], Goldman [38, 1926]), though this is not fully established, since the walls may produce intermediates which sensitize the gas-phase reaction.

(*d*) Increase of surface slows down the combustion.

(*e*) The temperature coefficient indicates that a very complicated sequence of events may be involved in a chain. This is most readily seen from results such as those of Dykstra and Edgar [26, 1934] or Prettre [73, 1932], where the higher paraffins are shown to undergo different modes of combustion at high or low temperatures. Owing to the fact that the temperature coefficient of the mode of combustion in the lower region becomes negative (Beatty and Edgar [4, 1934]), the separation into two regions is more clear-cut than in cases where there are two parallel reactions, and the relative importance of the reaction with higher activation energy increases at higher temperatures. Further reference to these two regions is made below. A parallel phenomenon has been described for the actual ignition temperatures (Townend [93, 1933, 1934]).

(*f*) The combustion of hydrocarbons with the possible exception of the more unsaturated molecules is autocatalytic. According to Semenoff [80*a*, 1935], the velocity of reaction increases at an exponential rate with time in the oxidation, e.g. of the paraffins, so that the rate passes through a maximum. Autocatalysis points to easily oxidized intermediates which by promoting the oxidation of the parent hydrocarbon are themselves reformed.

As in all chain reactions, the actual chain carriers are probably molecules too short-lived to be isolated (cf. Hinshelwood and Williamson [46, 1934] and p. 2946, this article). By comparing the oxidation of a pure hydrocarbon with that of possible intermediates, such as alcohols and aldehydes, a study of the kinetics can, however, show which intermediates are of importance in the degradation of a fuel to carbon dioxide and water. The importance of aldehydes and unimportance of alcohols for the higher paraffins have been shown by numerous workers, such as Layng and others [53, 1928], Pope, Dykstra, and Edgar [72, 1929], Pidgeon and Egerton [69, 1932]. In the same connexion Steacie and Plewes have shown that acetaldehyde has little influence on the rate of combustion of ethylene [87, 1934], which thus differs from ethane in its mechanism (Bone and Hill [13, 1930], but see Steacie and Plewes [88, 1934], Bone [13, 1934]).

Studies of the slow combustion of methane and ethane at pressures below 1 atmosphere have shown (Kowalsky, Sadownikow, and Tschirkow [51, 1932]) a change from slow combustion to ignition within certain regions of pressure, similar to the phenomena observed for H_2 (Hinshelwood and others [45, 1929–33]), though owing to the complexity of the possible products the phenomena are more complicated.

(*c*) Chemiluminescence.

The two modes of combustion exhibited by paraffins may be conveniently illustrated from the phenomena of chemiluminescence observed during slow combustion. If we expose a fuel mixture with excess of oxygen to a series of increasing temperatures, not much luminescence is observed till in the neighbourhood of the ignition point, which varies for different hydrocarbons and lies in the neighbourhood of 600° C. At the ignition point a faint luminescence is observed during the period of preflame, which may last several seconds. Spectroscopic studies show the flash is due to the production of a large number of ions and excited radicals such as CH, OH, &c., during the momentary high temperature resulting from the liberation of the heat of reaction (Bonhoeffer and Haber [17, 1928]). The phenomena of chemiluminescence are quite different and are specially marked for mixtures where the fuel is in excess (Prettre [73, 1932], Beatty and Edgar [4, 1934], Gill, Mardles, and Tett [37, 1928]).

As we gradually raise the temperature of a pentane mixture, for example, containing 6% of pentane, a definite luminescence is observed in the neighbourhood of 230° C., and becomes very intense about 240° C. Ignition does not set in till 260° C. If the temperature is raised above 290° C., however, the mixture no longer ignites, though strong luminescence is still visible. Ignition does not become possible again for this mixture till 710° C.

The following table, due to Prettre [73, 1932], illustrates the results for the different paraffins. The third column gives the interval below the first ignition point over which luminescence becomes increasingly marked, the fourth column the interval over which an ignition is possible in the low-temperature region, and the fifth the temperature at which ignition again becomes possible in the high-temperature region. In these observations the mixture flowed through the furnace at a uniform rate of 6 litres per hour.

Gas	%	*Lumins.*	*Lower ign.*	*Higher ign.*
CH_4	5·3	740°	. .	770° C. (CH_3OH inflames 540° C.)
	18·5	690°	. .	730° C.
C_2H_6	4·2	380–410°	. .	660° C.
	8·9	350–70°	. .	675° C.
C_3H_8	3·5	270–310°	. .	665° C.
	6·3	265–305°	. .	672° C.
	14·5	255–90°	304–10°	not possible
C_5H_{12}	2·1	242–60°	. .	670° C.
	4·05	221–40°	262–92°	681° C.
	16·55	225–44°	259–70°	not possible
C_6H_{14}	2·05	230–55°	. .	684° C.
	5·20	220–44°	255–70°	672° C.
C_7H_{16}	1·55	230–45°	. .	686° C.
	5·25	210–32°	259–69°	695° C.
C_8H_{18}	0·95	215–30°	. .	670° C.
	2·10	200–20°	252–70°	684° C.

The region over which ignition was observed at low temperatures compares with the values given by Dykstra and Edgar [26, 1934], and also by Townend [93, 1933, 1934], though differences are to be expected owing to the difference between a static and a flow method. Analysis of the combustion products with the heptane and heptenes used by Beatty and Edgar [4, 1934] shows that oxidation products are formed which are unexpectedly resistant to further oxidation below 350° C., but which have not been further specified.

There are several reasons why the phenomenon of chemiluminescence is important for the theory of slow combustion. In general, chemiluminescence is due to the formation of activated molecules, in this case in a chain process, and these molecules have time to emit their energy as radiation before it is dissipated as translational energy in a collision, or is used in propagating the chain. Spectrographic studies (Emeleus [30, 1926, 1929], cf. Fowler and Vaidya [32, 1931] for CS_2) have shown that the luminescent flames (called cool flames on account of the low temperature of the gases) of CH_3CHO, C_2H_5CHO, C_6H_{14}, and $(C_2H_5)_2O$ all give the same bands, thus suggesting a common origin and a common mechanism of low-temperature combustion for these substances (cf. Ubbelohde [94, 1935, part 1]).

The influence of impurities on the two zones of combustion is quite different. The high-temperature zone is relatively insensitive to the addition of small amounts of H_2, H_2O, or metallic anti-knocks. Although this insensitivity to anti-knocks may be due to the fact that at these high temperatures the equilibrium between two stages of oxidation of the anti-knock (Egerton [28, 1928]) is displaced too far one way, there is no doubt about the characteristic differences of behaviour of the low-temperature zone. The addition of metallic anti-knocks inhibits ignition and lessens luminescence; as little as 7% benzene in pentane has the same effect (Prettre [73, 1932]). Amyl nitrite, acetaldehyde, and to a lesser extent ethyl hydroperoxide increase the intensity of the phenomena without changing the temperature at which they are observed.

It is a significant fact that other substances showing marked chemiluminescence, such as ether and acetaldehyde, are strong knocking fuels, whereas the introduction of a double bond, of an OH or a COOH group which lower the knocking characteristics of a paraffin, likewise reduce the chemiluminescence markedly. The organic peroxides whose isolation has been reported by various authors (e.g. Mondain-Monval and Quanquin [62, 1931], Callendar [21, 1927], Egerton [28, 1927], Rideal and Brunner [77, 1928]), Ubbelohde [94, 1935] are usually obtained in this region of temperature.

(*d*) The Induction Period.

The short period of preflame in the high-temperature ignition zone has already been mentioned. In this zone the reaction may become autocatalytic on account of the fact that the heat of reaction cannot be dissipated sufficiently rapidly, so that the temperature and hence the rate increase to a very great degree. Phenomena of autocatalysis are also observed in the low-temperature zone, but are more marked on account of the different mechanism prevailing, probably with much longer chains.

When a combustible mixture is introduced into a clean reaction vessel at a suitable temperature, reaction does not always start as soon as the gas has reached the temperature of the enclosure. If the progress of the reaction be measured by the change in pressure, no change may be observed for half an hour or more, though once the reaction starts it proceeds smoothly. Analysis of the gases shows that no appreciable reaction has taken place, e.g. in the case of ethane (Bone and Hill [13, 1930], Bone and Allum [13, 1932]), though in the case of hexane Rideal and Brunner [77, 1928] and Brunner [20, 1930] were able to show that the apparent constancy of pressure did not indicate absence of all reaction, since peroxides and acids were formed during a period of constant pressure, and free oxygen was removed almost completely before a rapid rise in pressure set in (Fig. 2).

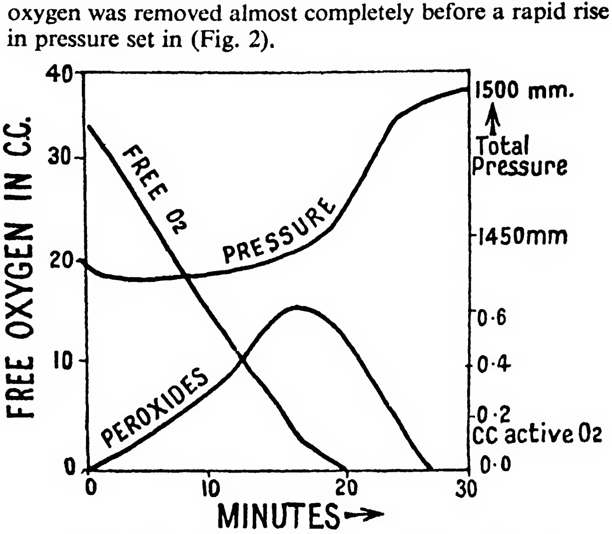


FIG. 2. Components of pressure-time curve. $C_6H_{14}+O_2$ at 210° C. (Rideal and Brunner).

The existence of an induction period indicates that the mixture must be sensitized in some way before combustion can proceed smoothly with rupture of the C–C bonds and rapid increase of pressure. The addition of certain sensitizers (Fig. 3) (CH_3CHO for ethylene, Steacie and Plewes [87, 1934], and H_2O, C_2H_5OH, I_2, HCHO, and NO_2 for ethane, Bone [13, 1930, 1932], Bone and Bell [11, 1934]) can greatly reduce or even eliminate the induction period, whereas the addition of mild anti-knocks such as aniline (Brunner [77, 1928; 20, 1930]) can greatly prolong it, and

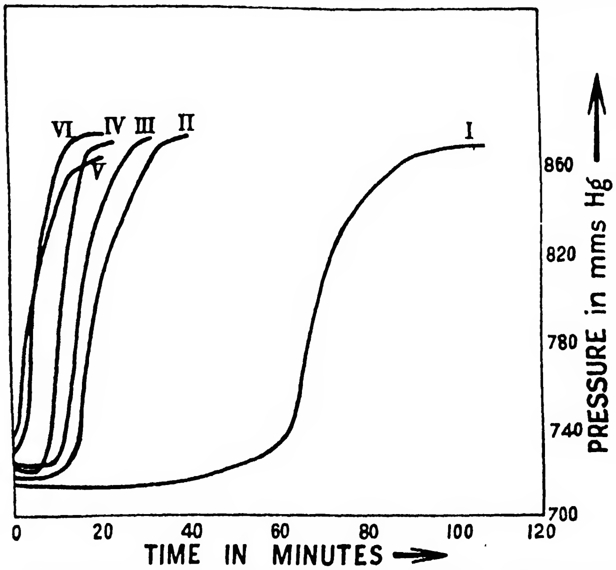


FIG. 3. Induction period and positive catalysts. $C_2H_6+O_2$ at 316° C. (Bone and Hill).

I. Dry mixture. III. 1% iodine. V. 1% NO_2.
II. 1% water. IV. 1% ethyl alcohol. VI. 1% HCHO.

may apparently inhibit the reaction altogether (Pidgeon and Egerton [69, 1932], Zeikowsky, Holroyd, and Sokoloff [102, 1929, 1930]). It is not yet clear whether the induction period implies the accumulation of sufficient sensitizers in the gas phase for the reaction to become autocatalytic, or whether the walls of the vessel are brought into a suitable state for initiating reaction chains. The undoubted influence of walls in initiating chain reactions in some cases (Haber and Alyea [41, 1930]) rather supports the second view, particularly in those cases where analysis of the gases confirms the fact that practically no reaction has taken place; only very small amounts of certain substances might sensitize the walls when adsorbed. The constancy of pressure observed by Rideal and Brunner [77, 1928] is due to a compensation of effects, and can hardly be called a true induction period.

(*e*) Wall Effects.

The effect of the walls on the slow combustion of hydrocarbons is quite characteristic. Increasing the wall surface by packing reduces the rate of reaction in all known cases. This is one of the reasons for assuming that chain reactions are effective in combustion, though the state of the walls may possibly control both the initiation and breaking of chains.

The state of the walls can be controlled in a number of ways:

(1) Repetition of a combustion in the same apparatus a number of times gradually brings them to a sufficiently standard condition to give a reproducible induction period, which is very erratic in a 'clean' vessel. Cf. Steacie and Plewes [87, 1934], Neumann and Egorow [67, 1932].

(2) Washing with suitable chemicals, e.g. HF aq., activates a quartz surface for the slow combustion of ethane to such a degree that reaction takes place at the same rate 150° lower (Kowalsky, Sadownikow, and Tschirkow [51, 1932]).

(3) Sintering or washing with alkali halides slows down hydrocarbon combustion in general, e.g. ethane, Kowalsky (l.c.); propane, butane, and H_2, Pease [68, 1929–34].

(*f*) Effect of Positive and Negative Catalysts on the Reactions.

The effect of small amounts of positive and negative catalysts on slow combustion is of considerable practical as well as theoretical importance. The principal negative catalysts for the low-temperature region of combustion are the metallic anti-knocks, which act in the engine by preventing slow combustion prior to the arrival of the flame. A number of positive catalysts have also been discovered, of which the most general in action is nitrogen peroxide. This catalyses the slow combustion and lowers the ignition temperature of various fuels such as hydrogen (Hinshelwood and others [45, 1928–9], Griffiths and Norrish [39, 1933]), methane (Smith and Milner [84, 1931]), ethane (Serbinov and Neuman [80, 1934]), acetylene (Lenher [54, 1931]), carbon monoxide (Kopp, Kowalsky, Sagulin, and Semenoff [50, 1930], Hinshelwood and Thompson [45, 1929]), isopentane and hexane (Lewis [55, 1930], and unpublished observations), alcohols (Mardles [58, 1928]), benzene (Bibb and Lucas [6, 1929]). This action of NO_2 is quite distinct from that of the pro-knock organic nitrites (Ubbelohde and Egerton [94, 1935], Mardles [58, 1928]), and NO_2 has under some conditions even an anti-knock effect. Its action in lessening the luminescence of CS_2 has been noted by Dixon [22, 1925]. These observations suggest that NO_2 sets up a different kind of chain mechanism in combustion, though its precise nature even in the case of hydrogen (Hinshelwood [45, 46]) has not been elucidated.

Owing to the fact that the presence of NO_2 lowers the temperatures at which slow oxidation can be observed by 100° or more in some cases, its use as a catalyst in the production of valuable intermediates from hydrocarbons suggests itself. In order to prevent the further oxidation of the intermediates, excess of hydrocarbon must be used, but the lower temperatures prevent the pyrolysis of oxidation products once they are formed (Smith and Milner [84, 1931], Bibb and Lucas [6, 1929]). There is evidence, however, that the NO_2 is consumed in the course of the reaction (cf. Gibson and Hinshelwood [36, 1928]).

The addition of aldehydes in many cases facilitates the combustion of hydrocarbons (Bone and Hill [13, 1930], Pidgeon and Egerton [69, 1932]) see Fig. 1, and since aldehydes are formed in the course of the combustion, the sensitization of combustible mixtures described under the induction period may involve merely the accumulation of sufficient aldehydes. The autocatalytic nature of most combustion reactions is likewise due in part to the acceleration of the process by the aldehydes formed (Egerton and Gates [28, 1927]). The induced oxidation of benzene, aniline, &c., at low temperatures, in the presence of oxidizing paraffins (Mardles [58, 1931]) is another aspect of the same phenomenon.

The effect of aldehydes in facilitating ignition (Egerton and Gates [28, 1927], Townend [93, 1934]) contrasts with their relatively slight pro-knock effect (Egerton, Llewellyn Smith, and Ubbelohde [28, 1935]); owing to the fact that acetaldehyde peroxide is a powerful pro-knock, it seems likely that the primary product of the slow oxidation of paraffins must be a different pro-knock, possibly a hydroperoxide (cf. Ubbelohde, Drinkwater, and Egerton [94, 1935]).

It is interesting to note that $PbEt_4$ before it is oxidized actually accelerates combustion (Pidgeon and Egerton [69, 1932]).

(*g*) Other Means of Studying Slow Combustion.

Any change in the physical properties of the mixture during combustion might in principle be used to study the rate at which it proceeds. One such method is based on the detection of intermediates with marked absorption spectra (Egerton and Pidgeon [28, 1933], Rassweiler and Withrow [75, 1932], Ubbelohde [94, 1935, part II]). Although the results must be correlated with other data to avoid misleading conclusions, the early formation of formaldehyde and the difference between the higher and lower paraffins in slow combustion at low temperatures is clearly brought out.

III. SUMMARY OF RESULTS WITH DIFFERENT FUELS

A brief summary of the results with the various fuels of importance for petroleum chemistry is necessary for an understanding of the theories of slow combustion. For this purpose the fuels will be divided as follows: (*a*) hydrogen, (*b*) carbon monoxide, (*c*) paraffins, (*d*) olefines, (*e*) acetylenes, (*f*) naphthenes, (*g*) aromatic hydrocarbons, (*h*) other substances relevant to petroleum chemistry. [Further details will be found in the article on Combustion of Hydrocarbons by D. M. Newitt and D. T. A. Townend, p. 2860.]

(*a*) Hydrogen and (*b*) Carbon Monoxide.

These fuels are included because they exhibit most of the phenomena of slow combustion, with the simplest possible molecules of fuel. They also occur as intermediates in certain combustions.

The data for hydrogen have been summarized by Hinshelwood and Williamson [46, 1934]. The only chemical products sufficiently stable to be isolated are H_2O and H_2O_2 (Pease [68, 1930]). The effect of washing the walls with dilute HNO_3 is to favour the formation of H_2O_2, and dilute KCl hinders it, a result which emphasizes the effect of pretreatment of the walls, observed in many slow combustions. The kinetics of the reaction have been repeatedly studied (Hinshelwood [45, 46, 1929–34]), and the effects of atomic hydrogen and oxygen investigated with a view to elucidating the mechanism (Bonhoeffer and Reichardt [18, 1928], Harteck and Kopsch [44, 1931], Frankenburger and Klinkhardt [33*a*, 1932]).

The reaction shows abundant evidence of a chain mechanism, with a low-pressure explosion region when the slow combustion becomes unstable owing to chain branching, and a high-pressure ignition when it becomes unstable owing to failure to dissipate the heat of reaction. No chemiluminescence has been recorded. Metastability phenomena analogous to an induction period have been described by Hadman, Thompson, and Hinshelwood [42, 1932]. The reaction is not much affected by metallic antiknocks (but see the effect of high temperatures on these, *supra*), and halogens act as negative catalysts (Garstang and Hinshelwood [35, 1931]). NO_2 is a positive catalyst (Gibson and Hinshelwood [36, 1928], Hinshelwood and Thompson [45, 1929], Griffiths and Norrish [39, 1933]), as are NH_3 and $(CN)_2$, or more probably some oxidation products (Williamson and Pickles [98, 1934]). Slow oxidation has been observed over an interval 450–600° in the absence of catalysts.

The slow oxidation of carbon monoxide is chiefly of importance in petroleum chemistry in that it is a frequent product of combustion, e.g. according to the scheme put forward for the octanes by Pope, Dykstra, and Edgar [72, 1929]

$$RCH_2CH_3+O_2 = RCH_2CHO+H_2O,$$

$$RCH_2CHO+O_2 = RCHO+CO+H_2O,$$

and

$$H_2CO = H_2+CO.$$

No slow combustion has been observed for CO much below 600°, so that it is a stable intermediate, unless produced in the high-temperature region of combustion, where it might affect the ignition considerably. CO_2 is the only stable product of slow combustion. The kinetics indicate a chain reaction with low-pressure region of explosion (Sagulin [79, 1928]). The luminescence in the region of preflame has been noted by Prettre and Laffitte [74, 1929] and Ubbelohde [94, 1933]. Both H_2 and H_2O are positive catalysts, in the slow combustion, and NO_2 is likewise active (Hadman, Thompson, and Hinshelwood [42, 1932], Sagulin [79, 1928]), and alkali halides are negative catalysts (Ubbelohde [94, 1933], Prettre [73*a*, 1932]).

(*c*) Paraffins.

In accordance with what has been said with reference to the two 'regions' of combustion of the higher paraffins, these may conveniently be classed into methane, ethane, and propane (which occupies an intermediary position), and the hydrocarbons from butane upwards.

The products which can be isolated during the slow combustion of methane and ethane are aldehydes, acids, CO, CO_2, and H_2O (cf. Bone [15, 12, 13, 1902–30], Bone and Townend [14, 1927], Bone and Allum [13, 1932], Bone and Hill [13, 1930]). The formation of alcohols is particularly noticeable when the reaction is carried out at higher pressures (Newitt and Haffner [65, 1932]). The products can be predicted from the hydroxylation theory of Bone:

$$\begin{array}{l}
CH_3-CH_3+\tfrac{1}{2}O_2 \rightarrow (CH_3CH_2OH)+\tfrac{1}{2}O_2\\
\quad\rightarrow CH_3CH(OH)_2 \rightarrow H_2O+CH_3CHO\\
\qquad\quad\downarrow\\
\qquad\quad CH_4+CO+H_2O\\
\quad\ +\tfrac{1}{2}O_2\\
\qquad\downarrow\\
CH_3OH+\tfrac{1}{2}O_2 \rightarrow CH_2(OH)_2 \rightarrow H_2O+HCHO+\tfrac{1}{2}O_2\\
\qquad\qquad\quad\downarrow \qquad\qquad\qquad\qquad\qquad\quad \downarrow\\
\qquad\qquad H_2+CO+H_2O \qquad\qquad\quad HCOOH
\end{array}$$

With propane, alcohols are obtained when the reaction is carried out at 136 atm. and 300–350° (Marek and Hahn [59, 1932]), a representative analysis of the liquid products being: CH_3CHO and CH_3COCH_3 6%; CH_3OH 22%; C_2H_5OH 37%; C_3H_7OH 7%; HCOOH 1·5%; H_2O 26·5%. A careful investigation of the products of slow combustion in a flow method at 1 atm. and 300–400° has also been made by Pease [68, 1934], who detected large amounts of organic peroxides under suitable conditions. Typical results are (in c.c. gas/400 c.c. reaction mixture):

c.c reacted: c.c. produced

Temp.	*Pr./*O_2	*Pr.*	O_2	C_3H_6	C_2H_4	H_2	CO	CO_2	*Pero.*	*Ald.*	*Def.*
400°	3/1	67	71	28	9	5	37	4	10	7	15
	1/3	41	74	13	..	..	28	5	9	1	26
(KCl)	1/3	25	45	10	2	7	16	6	trace	8	15

The walls of the pyrex combustion chamber were normally washed with nitric acid and distilled water, but quite different results with almost complete absence of peroxide formation were obtained if the walls were washed with dilute KCl (cf. Pease [68, 1930]). The formation of propene is significant with regard to theories of combustion. The last column refers to a deficit of carbon in the analysis due to the presence of a product presumably not allowed for.

The kinetics of the oxidation of methane have been studied by Bone (l.c.), and also by Pease and Chesebro [68, 1928], Hinshelwood and Fort [45, 1930], Kowalsky, Sadownikow, and Tschirkow [51, 1932]. Ethane has also been studied by Hinshelwood and Thompson [45, 1928–9], Taylor and Ribbet [90, 1931]. Propane has also been investigated by Pease [68, 1929], Sagulin [79, 1928], Burke, Fryling, and Schumann [20*a*, 1932]. The low-temperature oxidation shows the characteristic influence of excess fuel in catalysing the oxidation, the retarding effect due to dilution with O_2 or other gases becoming greater at higher temperatures (cf. Beatty and Edgar [4, 1934]). None of these gases show very marked chemiluminescence. An induction period can be observed under suitable conditions, and shows the normal effect of shortening by aldehydes, &c. The effect of NO_2 in facilitating the combustion of CH_4 and C_2H_6 has been described (Smith and Milner [84, 1931], Serbinov and Neumann [80, 1934]). No marked negative catalysts have been reported. The oxidation of methane by ozonized oxygen has been studied (Wheeler and Blair [96, 1922]).

The higher paraffins, from butane upwards, are characteristic in showing two modes of ignition. Combustion in the region below the lower ignition point has been investigated in a general way by Lewis [55, 1927–30], Pidgeon and Egerton [69, 1932], Mondain-Monval and Quanquin [62, 1931]. Butane has been investigated by Pease [68, 1929], hexane by Brunner [77, 1928; 20, 1928, 1930], the isomeric heptanes by Beatty and Edgar [4, 1934], and the isomeric octanes by Pope, Dykstra, and Edgar [72, 1929]. Hydrocarbons with still bigger chains have been oxidized in the liquid phase (Francis and Wood [33, 1922, 1927], Shoruigin and Kreshkov [82, 1934], Sheeley and King [81, 1934]) with a view to avoid breaking up the oxidation products by pyrolysis.

The experiments of Beatty and Edgar, and Pope, Dykstra, and Edgar are continued up to the higher region of temperatures.

If we consider the number of possible products which might be formed in an oxidation such as

$$C_5H_{12}+8O_2 = 5CO_2+6H_2O,$$

if the oxygen atoms entered each C–H bond successively, as the hydroxylation theory would postulate, the very complicated mixture would be difficult to investigate. Furthermore, if a hydrocarbon has several parallel modes of oxidation, a deduction of the oxidation mechanism from inspection of the products is difficult to substantiate. A considerable simplification is due to the work of Edgar and others [27, 72, 4, 1927, 1929, 1934], who have shown that in a long molecule the chief point of attack is the end methyl group. One mode of degradation of a hydrocarbon to CO_2 and water appears to follow the scheme

$$RCH_3+O_2 = (RCH_2OOH?) = RCHO+H_2O\ldots$$
$$RCH_2CHO+O_2 = RCHO+CO+H_2O.$$

In a branched hydrocarbon molecule the longest branch is attacked, and oxidation proceeds as above till the point of branching is reached. With straight chains the above degradation is said to hold down to butyraldehyde.

This relatively simple scheme clearly offers only one mode of oxidation; a survey of the experimental evidence does not make it clear whether other primary steps occur, or whether the very complicated mixture of products is due to the different modes of reaction of the aldehyde or peroxide. The complete inhibition of *all* oxidation by the addition of anti-knocks suggests that only one primary step occurs at low temperatures (Egerton, Llewellyn Smith, and Ubbelohde [28, 1935]).

The following products have been isolated from the slow oxidation of hexane *circa* 300° (Mondain-Monval and Quanquin [62, 1931]) (cf. Landa [52, 1928], Brunner and Rideal [77, 20, 1928, 1930], Wheeler and Blair [96, 1923], Mardles [58, 1928], Callendar [21, 1927]): aldehydes, chiefly formaldehyde, peroxides with the reactions of alcoxyperoxides R–O–O–CH_2(OH), giving hydrogen with strong alkali, acetals, and acids. The allyl compounds noted by Berl and Winnacker [5, 1928] were obtained in the slow oxidation of hexane over a contact mass of ferric oxide, so that the conditions are hardly comparable.

The kinetics of the oxidation of pentane and hexane have been studied by Pidgeon and Egerton [69, 1932], Mondain-Monval and Quanquin [62, 1931], and by Brunner and Rideal (l.c.). Owing to the complicated molecules involved, interpretation of rate of pressure rise, &c., in terms of a specific mechanism is difficult. As the results are very similar for these hydrocarbons, only those for pentane will be summarized here.

If the mixture is heated at a steady rate of 0·6° per minute from 210° (where there is no reaction over 90 minutes), the onset of rapid reaction is marked by a steep rise of the pressure/time curve, and the effect of fuel concentration, total pressure, and surface on the reaction temperature gives a measure of the importance of these factors in the kinetics.

The following are typical results:

Effect of total pressure on a 1:1 mixture of pentane/oxygen

P mm.	1,040	760	555	400	340
T	240	245	247	248	257°

Effect of concentration on reacting temperature
(pressure 540–90 mm.)

Conc. (pen./O_2)	1 : 6	1 : 3	1 : 1	2 : 1
T	260	251	247	250°

Effect of surface (1:1 mixture 800 mm.)

Surface	*Glass*		*Pyrex*	*Silica*
	131 sq. cm.	*462 sq. cm.*		*131 sq. cm.*
T	245	255	242	237°

These figures show that pressure increases the velocity, and that the optimum velocity is at a pentane/oxygen ratio 1:1 far above the theoretical 1:8. As may be expected from these results, which indicate chain breaking at the surface of the vessel, the addition of an inert gas (N_2) raises the velocity and lowers *T*. Very rapid heating prevents the formation of sensitizing intermediates, and raises *T* from 243° to 250° for a 1:1 mixture (slowest and fastest rates tried).

Experiments are also described (Pidgeon and Egerton, l.c.) on the effect of hydrocarbon and oxygen concentrations on the reaction velocity. As with most hydrocarbon combustions, increasing the concentration of fuel has a much larger effect than increasing the concentration of oxygen, suggesting the formation of a fuel/oxygen complex (moloxide) which must collide with another fuel molecule within a finite time for the chain to proceed. The temperature coefficient over the range 260–80° corresponds with an activation of 50,000 cal., but at lower temperatures lower values and erratic results suggest that this activation energy does not refer to a single process only (cf. Hinshelwood and Williamson on H_2+O_2 [46, 1934]).

Analysis shows that considerable amounts of CO and CO_2 are produced, as well as more complex products. With hexane, the pressure/time curve has been decomposed into the components: rate of removal of oxygen, rate of formation of acids, rate of formation of peroxides, and has shown the composite nature of pressure/time curves (Brunner, l.c.).

The kinetics of the oxidation of heptane, 2.2.4 trimethyl pentane, and *n*-octane have been studied by a flow method by Edgar and others [4, 72, 1929, 1934]. Typical results may be quoted for heptane. Using a 2% mixture (the theoretical mixture), at atmospheric pressure flowing through a clean pyrex tube, the following stages in the oxidation can be distinguished from a gas analysis of the products:

(1) 150–200°. Small possibly heterogeneous reaction.

(2) 250–350°. Primary reaction with rapidly increasing velocity, using 3 mols. O_2/mol. of fuel (lower ignition point with cold flames 270–300°).

(3) 350–470°. Subsequent reaction raises the O_2 consumption to 4·70 mols. per mol. fuel, which remains at this value over this temperature region. The velocity of both primary and subsequent reactions decreases rapidly with rise in temperature (temp. coeff. 0·85/10° rise from 380 to 470°).

(4) 470–510°. Velocity of primary reaction continues to decrease, but the subsequent reaction becomes faster, and above 490° the final amount of O_2 used is greater. Inflammation occurs about 490°.

The products are very complex, although the flow method has the advantage over static methods that products are exposed to high temperatures for a much shorter interval. It is almost impossible to experiment on heptane statically, owing to the resins produced.

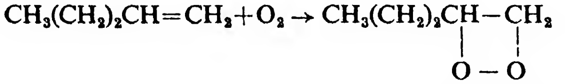
The same paper also describes the much greater stability of 2.2.4 trimethyl pentane to oxidation, no combustion being detected below 490° when this fuel was used pure, though in the presence of heptane very considerable oxidation resulted, suggesting that the difficulty of oxidation lies rather in the initiation of chains (see below).

All these fuels show the phenomenon of chemiluminescence and the induction period to a marked degree. Metallic anti-knocks inhibit oxidation at low temperatures (Pope, Dykstra, and Edgar [72, 1929], Lewis [55, 1927], Garner and Saunders [34, 1926]). The effect of NO_2 is probably similar to that on lower hydrocarbons (unpublished observations). All these hydrocarbons show a characteristic absorption spectrum at the end of the induction period, with a band at about 2,600 Å. (Egerton and Pidgeon [28, 1933]).

The mixture of products obtained from the slow oxidation of paraffins with a still greater number of carbon atoms has only been partly investigated (Francis [33, 1927], Shoruigin [82, 1934], Sheeley and King [81, 1934]), and consists of a complex mixture of hydroxy-acids and other compounds. The oxidation shows an induction period which is shortened by the addition of an easily oxidized substance such as turpentine (Francis).

(*d*) Olefines.

The mechanism of oxidation of the olefines is probably better understood than that of the paraffins, owing to the greater certainty about the primary step in their oxidation. Using the reagents described in a previous section, there is no difficulty in proving the ready autoxidation of the higher olefines such as amylene C_5H_{10}, by merely bubbling oxygen through the liquids at room temperatures, the reaction probably being



$$CH_3(CH_2)_2CH{=}CH_2+O_2 \rightarrow \begin{array}{c}CH_3(CH_2)_2CH-CH_2\\ \quad\quad\quad\quad\quad\quad | \quad\;\; | \\ \quad\quad\quad\quad\quad\quad O-O\end{array}$$

In many cases the peroxide is sufficiently stable for the reaction to stop at this stage (e.g. cyclohexene, Zelinsky and Borissov [103, 1930]), but on warming further decomposition and polymerization may take place (cf. Staudinger and Lautenschlager [86, 1931]).

At high temperatures, particularly when excess fuel is used, the formation of a similar peroxide as a first step is rendered very probable by the marked pressure drop observed (e.g. for amylene, Pidgeon and Egerton [69, 1932], Lewis [55, 1929]). With the simpler olefines, e.g. ethylene, a study of the kinetics suggests the formation of a similar peroxide as a first step, though the peroxides are in this case less easily isolated (Thompson and Hinshelwood [91, 1929], Spence and Taylor [85, 1930], Bone [16, 1934]). The subsequent oxidation follows on a collision with a second fuel molecule, after which the products probably follow the hydroxylation scheme

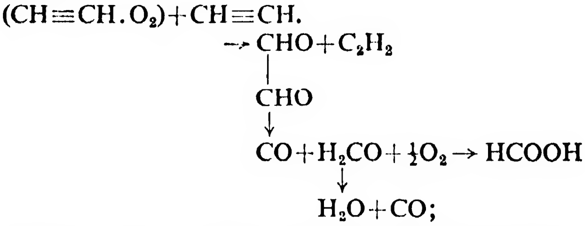
$$CH_2{=}CH_2+(CH_2{-}CH_2.O_2)\rightarrow$$
$$\rightarrow 2CH_2{=}CHOH \rightarrow \tfrac{1}{2}O_2 \rightarrow CHOH{=}CHOH$$
$$\swarrow\nearrow \quad \downarrow\uparrow \qquad\qquad\qquad \downarrow$$
$$(CH_2)_2O \qquad CH_3CHO \qquad\qquad 2HCHO \rightarrow$$
$$\rightarrow 2CO+2H_2, \text{ \&c.}$$

Lenher [54, 1931] obtained ethylene oxide, HCHO, and some H_2O_2 amongst the products of slow oxidation.

Although the olefines show an induction period, the absence of strong chemiluminescence (Prettre [73, 1932]) and the small influence of acetaldehyde on the combustion of ethylene (Steacie and Plewes [87, 1934]) suggest a different oxidation mechanism compared with the normal paraffins. This is borne out by the non-knocking characteristics of olefine peroxides (Ubbelohde and Egerton [94, 1935]). This difference is important, for it renders improbable one theory of hydrocarbon combustion (Lewis [55, 1927, 1929, 1930]) which postulates that the first stage for all hydrocarbons is some such process as $RCH_2CH_3 \rightarrow RCH{=}CH_2+H_2$, possibly catalysed by oxygen.

(*e*) Acetylenes.

The slow oxidation of acetylene has also been studied (Kistiakowsky and Lenher [49, 1930], Lenher [54, 1931]). Amongst the products which have been isolated is glyoxal; the rate is proportional to the square of the acetylene concentration and independent of the oxygen concentration over a region of pressures, which supports the reaction scheme



$$(CH{\equiv}CH.O_2)+CH{\equiv}CH.$$
$$\rightarrow \begin{array}{l}CHO+C_2H_2\\ |\\ CHO\end{array}$$
$$\downarrow$$
$$CO+H_2CO+\tfrac{1}{2}O_2 \rightarrow HCOOH$$
$$\downarrow$$
$$H_2O+CO;$$

cf. Bodenstein [9, 1931]. The formation of peroxides from acetylene has been reported (Young [100, 1934]).

(*f*) Naphthenes.

Although not many studies have been carried out on the oxidation of naphthenes, the process is probably very similar to that of the primary hydrocarbons, the only additional complication being the rupture of a C–C link at some stage of the oxidation, giving the product a fully aliphatic character. The slow oxidation of cyclopentane has been reported by Dupont [25, 1934], and of cyclohexane by Mardles [58, 1931], Berl and Winnacker [5, 1928].

(*g*) Aromatic Hydrocarbons.

The slow oxidation of aromatic hydrocarbons has the peculiarity that, once the benzene nucleus disrupts, very reactive and easily oxidized products are formed. The products of the slow oxidation may therefore be classified as follows:

(*a*) When side chains are present, attack begins on the α-carbon atom of the side chain (Stephens [89, 1926, 1928]), the first product with toluene being benzaldehyde. At high pressures benzyl alcohol is formed (Newitt and Szego [66, 1933] and Newitt and Burgoyne [66, 1936]).

(*b*) At high temperatures the formation of phenol and diphenyl has been reported (Weiss and Downs [95, 1920], Mardles [58, 1931]). Further oxidation leads to break-down products, of which maleic acid is an important component (Weiss and Downs [95, 1920]).

The kinetics have been studied by Fort and Hinshelwood [31, 1930] and Amiel [1*a*, 1933], and show the characteristic feature of hydrocarbon combustion in that a high power of the benzene concentration is involved in the equation for the reaction velocity, suggesting some intermediary moloxide even in this case. An apparent induction period may be due in part to the formation of first products without pressure increase. Chemiluminescence is not marked. The usual influence of NO_2 is observed (Bibb and Lucas [6, 1929]). Metallic anti-knocks have little effect (Garner and Saunders [34, 1926]). Although benzene when pure does not oxidize till a fairly high temperature (500° C.), in the presence of burning paraffins its oxidation proceeds at a much lower temperature (Mardles [58, 1928]), and a reduction of the chemiluminescence is observed (Prettre [73, 1932]).

(*h*) Alcohols, Aldehydes, &c.

The oxidation of these early intermediates in the degradation of a hydrocarbon is of considerable importance for the theory of combustion.

With regard to the alcohols, the general evidence is that they do not accelerate the combustion of hydrocarbons at low temperatures when mixtures are used in combustion (Pidgeon and Egerton [69, 1932], Mardles [58, 1931], Garner and Saunders [34, 1926]). The principal products of oxidation are probably the same as for the paraffins at higher temperatures, except that no peroxides have been isolated even with the higher alcohols (Ross and Ormandy [78, 1926]), nor are pro-knocks formed from them in the engine. Alcohols show the usual influence of NO_2 on combustion (Mardles [58, 1928]). Metallic anti-knocks have not much effect.

The oxidation of aldehydes is, on the other hand, of the greatest importance for the combustion of hydrocarbons. Numerous cases are known of aldehydes shortening the induction period (Bone [13, 1930, 1932], Steacie and Plewes [87, 1934]) and accelerating the combustion itself. The effect of metallic anti-knocks on the ignition of aldehydes is precisely parallel to that on paraffins (Egerton and Gates [28, 1927]), and aldehydes show a spectroscopically identical chemiluminescence (Emeleus [30, 1926, 1929]) at low temperatures. Furthermore, the mechanism of oxidation of aldehydes can be studied at a much lower temperature, so that complications due to pyrolysis are lessened. The kinetics of oxidation of aldehydes show very definitely a chain mechanism (Bodenstein [9, 1931], Backstrom [3, 1934], Hinshelwood and Fort [45, 1930], Askey [1*b*, 1930]) and throw a certain light on the nature of the chain carrier. Acids and peracids are the chief oxidation products. The oxidation of CH_3CHO can conveniently be demonstrated from the absorption spectrum (Egerton and Pidgeon [28, 1933]). The inhibitory effects of octenes on the oxidation of CH_3CHO have been reported (Pigulevsky [71, 1935]), also of alcohols and diphenylamine (Askey [1*b*, 1930], Pease [68, 1930]).

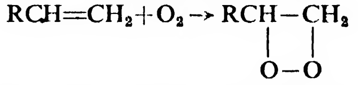
The oxidation of the possible intermediates from heptane, heptyl alcohol, heptaldehyde, and heptoic acid have been studied by Layng and Youker [53, 1928], and of heptaldehyde by Pope, Dykstra, and Edgar [72, 1929].

IV. THEORIES OF HYDROCARBON COMBUSTION

The object of this section must necessarily be to advance the principal facts and theories, since no entirely satisfactory theory of hydrocarbon combustion has yet been put forward. Summaries of the subject have been published at intervals: Bone and Townend [14, 1927], Egerton [28, 1928], Bodenstein [8, 1930], Bone [10, 1933], Egloff and Schaad [29, 1929], Milas [61, 1932], Marek and Hahn [59, 1932], Semenoff [80*a*, 1935], Norrish [64*a*, 1935], Ubbelohde [94, 1935]. The principal facts which need explanation may be listed as follows: (*a*) initiation of combustion, (*b*) nature of chain carriers, (*c*) stabilization of intermediates.

(*a*) Initiation of Combustion.

Evidence has been repeatedly quoted to show that, particularly at low temperatures, combustion is markedly autocatalytic, and may be preceded by a long induction period. Any theory of combustion must thus give some account of what is the primary act initiating combustion. With a saturated paraffin there are difficulties in proposing a solution of the problem which is satisfactory from energy considerations; with the olefines the situation is much clearer (*vide supra*), since there is very definite evidence for the formation of a peroxide by simple addition



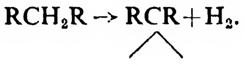
$$RCH{=}CH_2+O_2 \rightarrow \underset{\displaystyle O-O}{RCH-CH_2}$$

This fact led to the hypothesis that the first step in the oxidation of a saturated hydrocarbon was the elimination of H_2, since the resulting molecule could add on hydrogen without difficulty. Berl and Winnacker [5, 1928] put forward a modification of this idea, in that both hydrogen atoms are assumed to come off the same atom.

Lewis:

$$RCH_2CH_3 \rightarrow RCH{=}CH_2+H_2.$$

Berl and Winnacker:



$$RCH_2R \rightarrow \underset{\wedge}{RCR}+H_2.$$

From the velocity at which hydrocarbon pyrolysis takes place (Paul and Marek [67*b*, 1934]) and the energy required for the process of Berl and Winnacker (Discussion on Free Radicals [21*a*, 1934]), both these mechanisms seem very unlikely in the low-temperature region, unless they take place under the catalytic action of oxygen. Furthermore, the oxidation of an olefine does not follow the same course as that of a paraffin (Steacie and Plewes [88, 1934], Egerton and Pidgeon [28, 1932], Prettre [73, 1932]) and no pro-knocks are formed, so that the hypothesis does not seem to meet all the facts. At the same time, the isolation of propene in the slow combustion of propane (Pease [68, 1934]) shows that a process similar to that proposed by Lewis may occur in some cases. It should be noted, however, that the propene may be formed as the result of *ending* reaction chains, and the initiation of saturated paraffin combustion by olefines is certainly not proven.

A number of alternative views as to the nature of the primary step in oxidation have been proposed: (1) According to the hydroxylation theory, the primary step would involve a ternary collision $2RCH_3+O_2 = 2RCH_2(OH)$. On account of the large temperature coefficient of the reaction, such a process is, however, very unlikely. The production of alcohols at high pressures is probably the result of some stabilizing process at the end of a combustion chain, rather than the initiation of a chain, since the addition of alcohols has very little effect in stimulating combustion, and the higher alcohols seem to oxidize less easily than the corresponding hydrocarbons at low temperatures.

(2) Chains might be initiated from a collision with oxygen atoms, though at low temperatures the concentration of oxygen atoms would appear to be far too small for such a

process to occur at all frequently in the gas phase (Johnston and Walker [47, 1933]). Furthermore, Harteck and Kopsch [44, 1931] have shown that at ordinary temperatures not every collision of, e.g., CH_4 with O is efficient, so that a further activation is required. The high-temperature oxidation may possibly involve oxygen atoms in the chain. One test is to use ozone or ozonized oxygen for combustion, since in this case a reaction such as $RCH_3+O_3 = RCH_2(OH)+O_2$ does not involve a rupture of the O_2 molecule, and consequently requires far less activation. Experiments on the reaction between CH_4 and O_3 are indecisive, since $CH_3(OH)$ is much more easily oxidized than CH_4. With C_2H_6 ethyl alcohol has, however, been isolated (Drugman [23, 1906]), which supports the view that the failure of the hydroxylation theory with respect to initiation of combustion is due to the difficulty of rupturing O_2. For the action of ozone, cf. also Harries [43, 1905, 1910], Grün, Ulbrich, and Wirth [40, 1920], Taylor and Spence [90, 1930], Taylor and Ribbet [90, 1931].

A third way of avoiding the hypothesis that the initiation of combustion involves a rupture of the oxygen molecule, at any rate at low temperatures, is to assume the first step in oxidation is the process

$$RCH_3+O_2 \rightarrow RCH_2OOH \rightarrow RCHO+H_2O.$$

This assumption is the basis of a number of peroxide theories of combustion (Callendar [21, 1927], Egerton [28, 1927 and 1928], Moureu and Dufraisse [64, 1927], Stephens [89, 1933]), and has the following advantages:

(1) It explains the formation of aldehydes at a very early stage in combustion (Wheeler and Blair [96, 1923], Layng and Soukup [53, 1928], Callendar [21, 1927]).

(2) It explains the formation of an active pro-knock, which is not an aldehyde peroxide, as a very early stage in combustion (Egerton, Llewellyn Smith, and Ubbelohde [28, 1935], Ubbelohde, Drinkwater, and Egerton [94, 1935]).

(3) If the intermediate moloxide is unstable, it explains why practically all hydrocarbons require a collision with a second fuel molecule for the reaction to proceed.

(4) It explains why combustion is totally inhibited by anti-knocks, and does not even proceed to the aldehyde stage (Brunner [20, 1928, 1930], Egerton [28, 1928]), since besides acting on aldehyde peroxides anti-knocks act on alkyl peroxides. It must be remembered, on the other hand, that the isolation of peroxides during slow combustion (Brunner and Rideal [77, 20, 1928, 1930], Mondain-Monval and Quanquin [62, 1931]), and from a knocking explosion in an internal-combustion engine (Egerton and Ubbelohde [28, 1934]), does not prove that these stabilized products are chemically identical with the simple alkyl peroxides. These have been proved potent pro-knocks, whereas the peroxide isolated according to the technique of Mondain-Monval and Quanquin has only a mild pro-knock activity, which strongly suggests that it has a different structure (cf. Ubbelohde and Egerton [94, 1935]). Since added hydroperoxides have little effect on ignition and a great effect on knock, the rupture into radicals RO-¦-OH must involve activation of some kind.

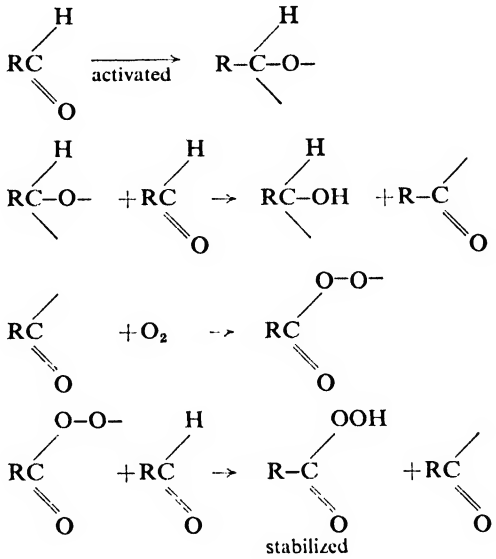
Finally, the very marked influence of surface on the induction period suggests that reaction chains may possibly be initiated on the surface, at any rate at low temperatures (cf. Goldman [38, 1926]). In this case the anti-knock might prevent the initiation of chains, or might act on the further oxidation of the aldehyde as well.

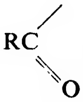
For the oxidation of solid carbon via peroxides see King [48, 1933].

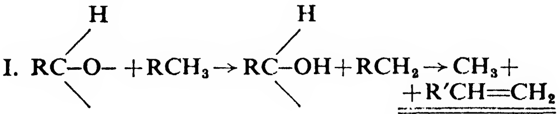
(*b*) **Chain Mechanism.**

The nature of the chain mechanism is likewise not fully elucidated for hydrocarbons, particularly for the low-temperature reaction. A number of points of attack are available:

The chain mechanism for paraffins is probably closely bound up with that for aldehydes, where autoxidation is easier to study both thermally and photochemically. According to Backstrom [3, 1934], the chain mechanism in aldehyde oxidation is of the type



The carrier is thus essentially the RC radical in this case. If the same radical is active in hydrocarbon combustion, the scheme might be extended as follows: (cf. Ubbelohde [94, 1935])



I. $R\overset{H}{C}{-}O{-} + RCH_3 \rightarrow R\overset{H}{C}{-}OH + RCH_2 \rightarrow CH_3 + \underline{\underline{+R'CH{=}CH_2}}$

(Cf. Rice [76, 1933].)

$$\text{II.}\;\begin{cases} RCH_2+O_2 \rightarrow RCH_2.O_2 \\ RCH_2O_2+RCH_3 \rightarrow \underline{\underline{RCH_2OOH}}+RCH_2 \end{cases}$$

$$\downarrow$$

$\underline{\underline{RCHO}}+H_2O$ (aldehyde catalyses the stage again)

$$\rightarrow RCH_2O+OH+RCH_2$$

(chain branching)

$$\text{III.}\;\begin{cases} OH+RH \rightarrow RCH_2+H_2O \\ RCH_2O+O_2 \rightarrow RO_2+\underline{\underline{CH_2O}} \end{cases}$$

This scheme has the advantage of explaining the following:

(1) The early appearance of formaldehyde and other aldehydes, which act autocatalytically.

(2) The appearance of a small amount of active pro-knock.

(3) A mechanism III of chain branching leading to ignition, when the conditions are suitable.

(4) The favourable effect of free alkyl radicals on combustion. Inhibitors probably stop the chain by combining

with $RCH_2{-}O{-}O{-}$, the product not being released again till it is oxidized.

A chain mechanism put forward by Semenoff in two alternative forms (see below) is adequate for explaining the kinetics at high temperatures, and illustrates the fact that the kinetics alone do not uniquely determine a mechanism of reaction (cf. Hinshelwood [46, 1934], Norrish [64*a*, 1935]).

$$\left.\begin{array}{l} CH_4O + O_2 \rightarrow CH_4O_2 + O \\ \qquad\qquad\qquad \downarrow \\ \qquad\qquad\qquad HCHO + H_2O \\ O + CH_4 \rightarrow CH_4O \end{array}\right\} \quad \text{I}$$

$$\begin{array}{ll} \text{or} & CH_4O + O_2 \rightarrow CH_4O_3 \text{ (unknown peroxide)} \\ & CH_4O_3 + CH_4 \rightarrow CH_4O + CH_4O_2 \\ & \qquad\qquad\qquad\qquad\qquad \downarrow \\ & \qquad\qquad\qquad\qquad\qquad HCHO + H_2O \end{array}$$

Alternatively,

$$\left.\begin{array}{ll} & CH_4O \rightarrow CH_2 + H_2O \\ & CH_2 + O_2 \rightarrow HCHO + O \\ & O + CH_4 \rightarrow H_2O + CH_2 \\ & \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot \\ \text{or} & CH_2 + O_2 \rightarrow CH_2O_2 \\ & CH_2O_2 + CH_4 \rightarrow HCHO + H_2O + CH_2 \end{array}\right\} \quad \text{II}$$

(*c*) Stabilized Products.

It follows from the above mechanism, or indeed from any chain mechanism, that the stable intermediates of combustion only bear an indirect relation to the actual reaction. It is for this reason that a theory such as the hydroxylation or even the peroxidation theory of hydrocarbon combustion is misleading if it claims to express the chain reaction solely in terms of products which are sufficiently stable to be isolated.

V. TRANSITION FROM SLOW COMBUSTION TO IGNITION

It has already been stated that the transition from slow combustion to ignition is of two kinds. At higher pressures the rate of reaction increases so rapidly that at a suitable temperature the heat of reaction can no longer be dissipated unless special vessels are used with large ratio of surface to volume. In consequence, the conditions no longer remain isothermal, and the reaction auto-accelerates, producing a very high temperature, and the characteristic emission of light from fragments of molecules such as are present in flames (Bonhoeffer and Haber [17, 1928]), CH, C–C, &c.

In the low-pressure region, which has only been studied carefully for H_2 (Hinshelwood and Williamson [46, 1934]), CO (Hinshelwood and others [45]), and CH_4 (Kowalsky, Sadownikow, and Tschirkow [51, 1932]), the transition from slow combustion to ignition is much sharper, owing to the fact that more chain carriers are produced than removed in unit time, by chain branching rather than by a gradual rise of temperature. Once the explosion sets in the rise in temperature due to the liberation of heat of reaction is very marked, however, and the characteristic luminosity observed in low-pressure explosions is probably spectroscopically similar to that of flames, though this has not been tested.

The bearing of these views on the ignition mechanisms in the internal combustion engine may be summarized as follows: In the spark-ignition engine, active centres are produced by the energy of the spark and, if the mixture is suitable, the thermal conditions in the resulting flame front are such that a region of ignition can proceed through the mixture. Owing to the fact that active centres are shot out from the flame front into the unburnt mixture, the ignition of successive layers does not necessarily involve their being raised to the static ignition temperature by conduction from the flame front (cf. Garner and Saunders [34, 1925], Lewis and von Elbe [56, 1934]). This explains why the addition of small amounts of pro-knocks (e.g. 10^{-5} mol fraction) has a relatively small effect on static ignition temperatures, but leads to a strong knock in the engine cylinder. In the same way, in the absence of added pro-knocks, slow oxidation of the last portion of the charge to burn sensitizes the mixture, so that on approach of the flame front the mixture is suddenly ignited as a whole, chain branching setting out from all the active centres present. The olefines do not lend themselves to this type of branching, and so are not pro-knocks, in spite of their very easy peroxidation (Ubbelohde and Egerton [94, 1935]).

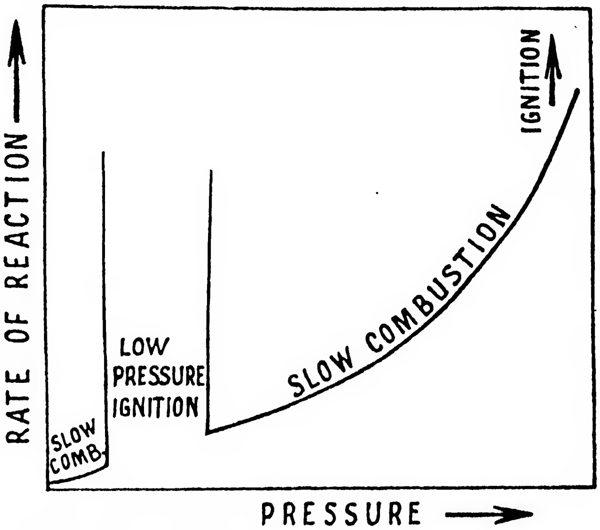


FIG. 4. Transition from slow combustion to ignition at low and high pressures.

In the compression ignition engine, on the other hand, ignition begins when the reaction velocity is sufficiently large. This is conditioned partly by the heat of adiabatic compression, but also by the ease with which various fuels are oxidized, even at low temperatures, thus liberating the heat of reaction and upsetting the temperature balance still more. With fuels whose velocity of combustion is small at low temperatures and which show marked induction periods, ignition is very sudden and rough, but the addition of small amounts of chain initiators such as amyl nitrite gives a much smoother and more gradual transition from slow combustion to ignition (cf. Lewis [55, 1930]).

REFERENCES

1. ALILAIRE. *Compt. rend.* **168,** 729 (1917).
1*a*. AMIEL, J. *Compt. rend.* **197,** 984 (1933).
1*b*. ASKEY, P. J. *J.A.C.S.* **52,** 974 (1930).
2. AUBERT, M., PIGNOT, A., and VILLAY, J. *Compt. rend.* **185,** 1111 (1927).
3. BACKSTROM. *Z. Phys. Chem.* **25B,** 99 (1934).
4. BEATTY, H. A., and EDGAR, G. *J.A.C.S.* **56,** 102 (1934).
5. BERL, E., and WINNACKER, K. *Z. Phys. Chem.* **139A,** 453 (1928); **145A,** 161 (1929); **148A,** 36, 261 (1930).
6. BIBB, C. H., and LUCAS, H. J. *Ind. Eng. Chem.* **21,** 635 (1929).

7. Blair, E. W., and Wheeler, T. S. *J.S.C.I.* **42,** 415 (1923).
8. Bodenstein, M. *Chem. Rev.* **7,** 220 (1930).
9. —— *Z. Phys. Chem.* **128,** 151 (1931).
10. Bone, W. A. Bakerian Lecture, 1933, *J.C.S.* 1599.
11. Bone, W. A., and Bell, J. *Proc. Roy. Soc.* **144 A,** 257 (1934).
12. Bone, W. A., and Drugman, J. *Proc. Chem. Soc.* **20,** 127 (1904).
13. Bone, W. A., and Hill, S. G. *Proc. Roy. Soc.* **129 A,** 434 (1930).
    Bone, W. A. *Chem. and Ind.* 962 (1934).
    Bone, W. A., and Allum, R. E. *Proc. Roy. Soc.* **134 A,** 591 (1932).
14. Bone, W. A., and Townend, D. T. A. *Flame and Combustion in Gases* (1927).
15. Bone, W. A., and Wheeler, W. H. *J.C.S.* 535 (1902); 1074 (1903); 1637 (1905).
    Bone, W. A., and Stockings, W. E. *J.C.S.* 693 (1904).
    Bone, W. A., and Andrew, G. W. *J.C.S.* 1232 (1905).
    Bone, W. A. *Phil. Trans. Roy. Soc., A,* **215,** 275 (1915).
16. Bone, W. A., Haffner, A. E., and Rance, H. F. *Proc. Roy. Soc.* **143 A,** 16 (1934).
17. Bonhoeffer, K. F., and Haber, F. *Z. Phys. Chem.* **137 A,** 263 (1928).
18. Bonhoeffer, K. F., and Reichardt, A. *Z. Phys. Chem.* **139 A,** 75 (1928).
19. Boord, R. E., and Schaad, C. E. *Ind. Eng. Chem.* **21,** 756 (1929).
20. Brunner, M. *Helv. Chim. Act.* **10,** 707 (1927); **11,** 881 (1928); **13,** 197 (1930).
20*a*. Burke, S. P., Fryling, C. F., and Schumann, T. E. W. *Ind. Eng. Chem.* **24,** 804 (1932).
21. Callendar, H. L. *Engineering,* **123,** 147, 182, 210 (1927).
21*a*. Discussion on Free Radicals. *Trans. Faraday Soc.* **30,** 1 (1934).
22. Dixon, H. B. *Rec. Trav. Chim. Pays-Bas,* **44,** 305 (1925).
    Dixon, H. B., Higgins, W. F., and Harwood, J. *Trans. Faraday Soc.* **22,** 267 (1926).
    Dixon, H. B., and Coward, H. F. *J.C.S.* 1382 (1934).
23. Drugman, J. *J.C.S.* 939 (1906).
24. Dumanois, P., and Mondain-Monval. *Compt. rend.* **187,** 892 (1928); *Ann. Comb. Liq.* **3,** 761 (1929).
25. Dupont, P. *Bull. Soc. Chim. Belg.* **43,** 537 (1934).
26. Dykstra, F. J., and Edgar, G. *Ind. Eng. Chem.* **26,** 509 (1934).
27. Edgar, G. *Ind. Eng. Chem.* **19,** 145 (1927).
28. Egerton, A., and Gates, S. F. *J.I.P.T.* **13,** 256 (1927) and *Aero. Res. Comm.* 1079 (1927).
    Egerton, A. *Nature,* **21,** 10 (1928).
    Egerton, A., and Pidgeon, L. M. *Proc. Roy. Soc.* **142 A,** 26 (1933).
    Egerton, A., and Ubbelohde, A. R. *Nature,* **133,** 179 (1934).
    Egerton, A., Llewellyn Smith, and Ubbelohde, A. R. *Phil. Trans. Roy. Soc.* 1935.
29. Egloff, G., and Schaad, C. E. *Chem. Rev.* **6,** 91 (1929).
30. Emeleus, H. J. *J.C.S.* 2948 (1926); 1733 (1929).
31. Fort, R., and Hinshelwood, C. N. *Proc. Roy. Soc.* **127 A,** 218 (1930).
32. Fowler, A., and Vaidya, W. M. *Proc. Roy. Soc.* **132 A,** 310 (1931).
33. Francis, F., and Wood, N. E. *J.C.S.* 501 (1922); 1897 (1927).
33*a*. Frankenburger, W., and Klinkhardt, H. *Z. Phys. Chem.* **15 B,** 421 (1932).
34. Garner, W. E., and Saunders, S. W. *J.C.S.* **127,** 77 (1925); *Trans. Faraday Soc.* 333 (1926).
35. Garstang, W. L., and Hinshelwood, C. N. *Proc. Roy. Soc.* **130 A,** 640 (1931).
36. Gibson, C. H., and Hinshelwood, C. N. *Trans. Faraday Soc.* **24,** 559 (1928). *Proc. Roy. Soc.* **119 A,** 591 (1928).
37. Gill, F., Mardles, E. W. J., and Tett, H. C. *Trans. Faraday Soc.* **24,** 574 (1928).
38. Goldman. *Z. Phys. Chem.* **5 B,** 316 (1926).
39. Griffiths, J. G. A., and Norrish, R. G. W. *Proc. Roy. Soc.* **139 A,** 147 (1933).
40. Grün, A., Ulbrich, E., and Wirth, T. *Ber.* **53,** 987 (1920).
41. Haber, F., and Alyea, H. N. *Z. Phys. Chem.* **10 B,** 193 (1930).
42. Hadman, G., Thompson, H. W., and Hinshelwood, C. N. *Proc. Roy. Soc.* **137 A,** 97 (1932); **138 A,** 297 (1932).
43. Harries, D. *Ann.* **343,** 11 (1905); **374,** 288 (1910).
44. Harteck. P., and Kopsch, U. *Z. Phys. Chem.* **12 B,** 327 (1931).
45. Hinshelwood, C. N., and Thompson, H. W. *Proc. Roy. Soc.* **118 A,** 170 (1928); **122 A,** 610 (1929); **124 A,** 219 (1929).
    Hinshelwood, C. N., and Fort, R. *Proc. Roy. Soc.* **129 A,** 284 (1930).
    Hinshelwood, C. N., and Moelwyn Hughes. *Proc. Roy. Soc.* **138 A,** 311 (1932).
    Hinshelwood, C. N., and Grant, G. H. *Proc. Roy. Soc.* **141 A,** 29 (1933).
46. Hinshelwood, C. N., and Williamson. *The Reaction between Hydrogen and Oxygen* (1934).
47. Johnston, H. M., and Walker, L. K. *J.A.C.S.* **55,** 187 (1933).
48. King, A. *J.C.S.* 842 (1933).
49. Kistiakowsky, G. B., and Lenher, S. *J.A.C.S.* **52,** 3785 (1930).
50. Kopp, D. L. A., Kowalsky, A., Sagulin, A. B., and Semenoff, N. *Z. Phys. Chem.* **6 B,** 307 (1930).
51. Kowalsky, A., Sadownikow, and Tschirkow. *Z. Phys. Sowjt. Un.* **1,** 451, 567 (1932).
52. Landa, S. *Compt. rend.* **186,** 589 (1928).
53. Layng, T. E., and Youker, M. A. *Ind. Eng. Chem.* **20,** 1049 (1928).
    Layng, T. E., and Soukup, R. *Ind. Eng. Chem.* **20,** 1052 (1928).
54. Lenher, S. *J.A.C.S.* **53,** 2962 (1931); **53,** 3737, 3752 (1931).
55. Lewis, B. *J.C.S.* 1555 (1927); 759 (1929); **58,** 2241 (1930).
56. Lewis, B., and Elbe, G. von. *J. Chem. Phys.* **2,** 537 (1934).
56*a*. Lovell, W. G., Collman, J. D., and Boyd, T. A. *Ind. Eng. Chem.* **18,** 373 (1927).
57. Mallard and Le Chatelier, H. *Ann. Mines,* iv. **8,** 274–618 (1913).
57*a*. Manning, A. B., King, J. G., and Sinnat, F. S. *Fuel Res. Tech. Paper* 19, Dep. Sci. Ind. Res. 1928.
58. Mardles, E. W. J. *J.C.S.* 872 (1928); *Trans. Faraday Soc.* **27,** 681 (1931).
59. Marek, I., and Hahn. *Catalytic Oxidation in the Vapour Phase* (1932).
60. Mason, W., and Wheeler, R. V. *J.C.S.* 2079 (1922); 1869 (1924).
61. Milas, N. A. *Chem. Rev.* **10,** 295 (1932).
62. Mondain-Monval, P., and Quanquin, B. *Compt. rend.* **189,** 917, 1194 (1929); **191,** 299 (1930); *Ann. Comb. Liq.* **5,** 307 (1930); *Ann. Chim.* **15,** 307 (1931).
63. Moore, H. *J.S.C.I.* **36,** 109 (1917); *J.I.P.T.* **6,** 186 (1920).
64. Moureu, C., and Dufraisse, C. *Compt. rend.* **185,** 1545 (1927); **186,** 196 (1928).
64*a*. Norrish, R. G. W. *Proc. Roy. Soc.* **150 A,** 36 (1935).
65. Newitt, D. M., and Haffner, A. E. *Proc. Roy. Soc.* **134 A,** 591 (1932).
66. Newitt, D. M., and Szego, P. *Chem. and Ind.* 645 (1933).
    Newitt, D. M., and Burgoyne. *Proc. Roy. Soc.* 448 (1936), 153 A.
67. Neumann, M. B., and Egorow, L. N. *Phys. Z. Sowjt. Un.* **1,** 700 (1932).
67*a*. Neumann, M., and Serbinov, A. *Nature,* **128,** 1040 (1931).
67*b*. Paul, R. E., and Marek, L. F. *Ind. Eng. Chem.* **26,** 454 (1934).
68. Pease, R. N., and Chesebro, P. R. *Proc. Nat. Acad. Sci.* **14,** 472 (1928).
    Pease, R. N. *J.A.C.S.* **51,** 1839 (1929); **52,** 5106 (1930); **55,** 2753 (1933); **56,** 2034 (1934).
69. Pidgeon, L. M., and Egerton, A. *J.C.S.* 661 (1932).
70. Pignot, A. *Compt. rend.* **182,** 376 (1926).
71. Pigulevski. *Brit. Chem. Abstr.* 1329 A (1934).
72. Pope, J. C., Dykstra, F. J., and Edgar, G. *J.A.C.S.* **51,** 1875, 2203, 2213 (1929).
73. Prettre, M. *Ann. Comb. Liq.* **6,** 7, 269, 533 (1931); **7,** 699 (1932); *Bull. Soc. Chim. Franç.* **51,** 1132 (1932).
73*a*. —— *Mem. Poudres,* **25,** 160 (1932).
74. Prettre, M., and Laffitte. *Compt. rend.* **189,** 177 (1929).
    Prettre, M., Dumanois, P., and Laffitte. *Compt. rend.* **191,** 329, 414 (1930).
    Prettre, M., and Laffitte, P. *Bull. Soc. Chim. Franç.* **45,** 785 (1929).
75. Rassweiler, G. M., and Withrow, L. *Ind. Eng. Chem.* **24,** 528 (1932).
76. Rice. *Trans. Faraday Soc.* **30,** 152 (1933).
77. Rideal, E. K., and Brunner, M. *J.C.S.* 1162, 2824 (1928).
78. Ross and Ormandy. *J.S.C.I.* 273 (1926).
79. Sagulin, A. B. *Z. Phys. Chem.* **1 B,** 275 (1928).
    Sagulin, A. B., and Semenoff, N. *Z. Phys. Chem.* **6 B,** 307 (1930).
80. Serbinov, A., and Neumann, M. *Compt. rend. Ac. Sci. U.S.S.R.* **2,** 297 (1934); *Brit. Chem. Abstr.* 737 A (1934).
80*a*. Semenoff, N. *Chemical Kinetics and Chain Reactions* (1935).
81. Sheeley, C. Q., and King, W. H. *Ind. Eng. Chem.* **26,** 1150 (1934).
82. Shoruigin and Kreshkov. *Chem. Abstr.* **28,** 6106 (1934).
83. Sinnot and Moore. *J.S.C.I.* **39,** 72 (1918).
84. Smith, D. F., and Milner, R. T. *Ind. Eng. Chem.* **23,** 357 (1931).
85. Spence, R., and Taylor, H. S. *J.A.C.S.* **52,** 2399 (1930).
86. Staudinger, H., and Lautenschlager. *Ann.* **488,** 1 (1931).
87. Steacie, E. W. R., and Plewes, A. C. *Proc. Roy. Soc.* **146 A,** 72 (1934).
88. —— —— *Proc. Roy. Soc.* **146 A,** 583 (1934).

89. Stephens, H. N. *J.A.C.S.* **48,** 1824 (1926); **50,** 2523 (1928); *J. Phys. Chem.* **37,** 209 (1933); **38,** 411 (1933).

90. Taylor, H. S. *Trans. Faraday Soc.* **21,** 560 (1926).
Taylor, H. S., and Spence, R. *J.A.C.S.* **52,** 2399 (1930).
Taylor, H. S., and Ribbet. *J. Phys. Chem.* **35,** 2667 (1931).

91. Thompson, H. W., and Hinshelwood, C. N. *Proc. Roy. Soc.* **125** A, 277 (1929).

92. Tizard, H., and Pye, D. R. *Phil. Mag.* **44,** 79 (1922); **1,** 1094 (1926).

93. Townend, D. T. A., and Mandlekar, M. R. *Proc. Roy. Soc.* **141** A, 484 (1933).
Townend, D. T. A. *Proc. Roy. Soc.* **143** A, 168 (1933).
Townend, D. T. A., Cohen, L. L., and Mandlekar, M. R. *Proc. Roy. Soc.* **146** A, 113 (1934).

94. Ubbelohde, A. R. *J.C.S.* 972 (1933).
Ubbelohde, A. R., and Egerton, A. *Nature,* **135,** 67 (1935).
Ubbelohde, A. R. *Proc. Roy. Soc.* **152** A, 354 (1935) part I and part II.
Ubbelohde, A. R., Drinkwater, and Egerton, A. *Proc. Roy. Soc.* **153** A (1935).

94*a*. Vorlander, D. *Z. An. Chem.* **77,** 241 (1929).

95. Weiss and Downs. *Ind. Eng. Chem.* **12,** 288 (1920); *J.S.C.I.* 45, 193 (1926).

96. Wheeler and Blair. *J.S.C.I.* 303 (1922); 81, 419, 491 (1923).

97. White, A. G., and Price, T. W. *J.C.S.* **115,** 1462 (1919).

98. Williamson, A. T., and Pickles, N. J. T. *Trans. Faraday Soc.* 30, 926 (1934).

99. Withrow, L., Lovell, W. G., and Boyd, T. A. *Ind. Eng. Chem.* **22,** 945 (1930).
Withrow, L., and Rassweiler, G. M. *Ind. Eng. Chem.* **25,** 923 (1933).

100. Young, P. L. *J.A.C.S.* **56,** 1822 (1934).

101. Yule, J. A. C., and Wilson, C. P. *Ind. Eng. Chem.* **23,** 1254 (1931).

102. Zeikowsky, Holroyd, and Sokoloff. *Phys. Rev.* **33,** 264 (1929); *Chem. Abstr.* **24,** 4620 (1930).

103. Zelinsky, N. D., and Borissov, P. P. *Ber.* **60,** 2362 (1930).

4. THE SUSCEPTIBILITY TO OXIDATION OF INTERNAL-COMBUSTION ENGINE FUELS AND THEIR TENDENCY TO PRODUCE KNOCKING IN ENGINES

By M. PRETTRE

THE improvements that have taken place in the design of I.C. engines have made the choice of fuel of the utmost importance. In all engines better mechanical efficiency has been obtained by the use of high-compression ratios, but these ratios are limited by the extent of the knocking produced. Each particular fuel has its own characteristic tendency to cause knocking; fuels are classified by their knock-producing tendencies, as measured by the various methods in use: e.g. H.U.C.R. of Ricardo [39, 1923], the octane number of Edgar [14, 1927], or the aniline equivalent of Lovell, Campbell, and Boyd [24, 1931, 1933–4].

In a similar manner compression-ignition or injection engines are sensitive to the fuel used, such that it is necessary to classify them, and in this case the cetene number is determined (Boerlage and Broeze) [3, 1931].

All these classifications show the influence of the chemical nature of the fuel on the functioning of engines. Two hypotheses have been put forward in order to explain this influence: either the flame region varies greatly with the nature of the explosion mixture under the conditions in the engine (a high pressure and a temperature well above 100° C., such variations being provoked by the electric spark in the case of I.C. engines) or, in spite of the very short time that the mixture is in the cylinder, it undergoes a change of chemical constitution under the conditions of temperature and pressure obtained. There results from this important change an explosion phenomenon different from that caused by ignition of the initial mixture.

A study of the propagation of explosion in the detonation and deflagration region with different mixtures has shown that under the conditions employed variations in the chemical constitution of the mixture in the explosion region due to the effect of the spark do not appear to be enough to account for the variations in the knocking tendencies (see Article 9).

On the other hand, recent work on oxidation and spontaneous ignition of air and hydrocarbon vapour mixtures at ordinary temperatures have shown that the extent of oxidation of the hydrocarbons varies in a similar manner to their knock-producing properties.

Early systematic studies on oxidation of the paraffinic hydrocarbons indicate that these reactions reach an appreciable velocity at about 400 to 500° C. (Bone [4, 1927, 1929], and Wheeler [49, 1918, 1922]), and that ignition took place at atmospheric pressure (Mason and Wheeler [26, 1922, 1924]), as well as at increased pressures and at 500° C. (Dixon [9, 1920]). The only substances used for these experiments were gaseous or very volatile at ordinary temperatures; the higher homologues were never examined. In 1922 Tizard and Pye [46, 1922, 1926] stated that higher homologues were more readily oxidized; they obtained spontaneous ignition of hexane, heptane, and octane mixtures with air under adiabatic compression at temperatures in the neighbourhood of 300° C. under a pressure of 5 atm., with a delay period of less than 1 sec. Some years later numerous investigations showed that the paraffinic hydrocarbons could be readily oxidized at 200° C. under atmospheric pressure, and that spontaneous ignition temperatures of such mixtures were less than 300° C.

Oxidation of Hydrocarbons at 200° C.

Early investigations on this subject were carried out by Callendar [6, 1927], and by Moureu [30, 1927]; the first named found that for each mixture there was an initial combustion temperature, characterized by the formation of water vapour, carbon dioxide, and substances of a peroxide type. These temperatures increased regularly on passing from the lower homologues to those higher in the series, e.g. pentane 295° C., hexane 265° C., undecane 200° C. The benzene type of hydrocarbons were only oxidized in a comparable manner at a temperature of about 500° C. Moureu showed that the oxygen absorption velocities of paraffins, petrols, hydronapthalenes, and numerous oils were very appreciable at 160° C. The reaction implied the formation of peroxides, and was sensitive to the action of numerous inhibitors, termed by Moureu 'Antioxydants'. At higher pressures the oxidation was again more pronounced. Lewis [23, 1927, 1929–30] burned various mixtures of hydrocarbons and oxygen in a closed vessel commencing at ordinary temperatures and pressures, and heating up to about 300° C. A curve of the pressure as a function of the normal temperature showed a sudden increase at a definite temperature (the Critical Inflexion Temperature or C.I.T.). The position and importance of this inflexion was found to depend on the nature of the mixture, on its concentration and velocity of burning. The C.I.T. was lowered for each mixture with an increase in the initial concentration of the combustible portion; it was also lowered as the homologous series was ascended (cf. the T.I.C. of Callendar), e.g. pentane 255° C., 135 cm. pressure, octane 200° C., 130 cm. pressure.

Dumanois and Mondain-Monval [12, 1928] have carried out similar experiments but commencing at pressures of about 6 kg. at ordinary temperatures. The temperatures for which the oxidation velocity becomes important are a little lower than those obtained by Lewis, the pressures being higher. Further, these authors have differentiated between results with weak and rich mixtures. In the case of pentane there was a rapid increase of pressure at 250° C.; richer mixtures reacted slowly at first with a contraction in volume from 120 to 130° C., and then more rapidly and completely at 230–40° C.; this latter reaction led to explosion within certain concentration limits. Mondain-Monval [28, 1929–30] and Quanquin [38, 1931] obtained comparable results with other paraffinic hydrocarbons. Here again, the temperature at which there was rapid oxidation accompanied by burning decreased from pentane 235 to 229° C., according to the quantity of air present, to octane 226–215° C. Mondain-Monval [29, 1933, 1935] and Wellard [48, 1935] have stated the influence of the velocity of heating on the phenomenon of slow, or explosive, combustion observed under these conditions.

These foregoing investigations are sufficient to show the great oxidizability above 200° C. of paraffin hydrocarbon vapours which constitute the major part of the usual fuels. They also show the accelerating effect of pressure.

Researches by various authors have shown that most organic vapours are easily oxidized from 200 to 300° C. Reference should be made to the work of the following authors: Berl [1], Pope, Dykstra, and Edgar [34, 1929], Mardles [25, 1928, 1931–2], Egerton [15, 1927–8], Bodenstein [2, 1931–2], Spence [43, 1928], Brunner and Rideal [5, 1928], and Mlle Estradère [18].

Spontaneous Ignition of Hydrocarbons between 250 and 300° C.

(*a*) **Ignition at Atmospheric Pressure.** It is possible to obtain spontaneous ignition, at about 250° C. under ordinary pressures, of all paraffinic hydrocarbons containing at least three carbon atoms in the molecule, e.g. propane and homologues, under the following conditions (Prettre, Dumanois, and Laffitte [37, 1930], Prettre [35, 1931]). The hydrocarbon mixtures containing an excess of the hydrocarbon were caused to flow at 4–12 litres per hr. (at N.T.P.) at constant temperature through a vessel of 200° c.c. capacity; the temperature of the latter could be increased from 20 to 700° C. In the case of hexane the following phenomena as a function of the temperature were observed. There was no measurable oxidation at 200° C., but at 245° C. reaction began; there appeared simultaneously in the combustion vessel a luminescence, or cold flame. This latter increased in intensity with the temperature, as did the oxidation velocity. At 245° C. the cold flame was accompanied by exothermic phenomena, detectable by the thermometer, and the gas escaping from the area of combustion no longer contained molecules of the hydrocarbon intact. At 255° C. an explosion set in, but not of a violent type, because the flow of gas employed was small and the fresh mixture became diluted by the already oxidized gas. At this temperature a true flame was obtained and no longer a cold flame, as at the lower temperatures.

As the temperature continued to increase above 255° C., a succession of explosions was obtained at definite time-intervals, which gradually diminished as did the violence of the explosions. At 275° C. a true flame was no longer produced, but a new cold flame, less intense than that produced before spontaneous ignition of the mixture, took place. Finally, at a temperature generally above 650° C. spontaneous ignition again occurred.

These results establish that at ordinary pressures certain fuel mixtures, i.e. those which easily produce knocking in engines, ignite not only at temperatures greater than a certain value, e.g. 500°, 600°, or 650° C., depending on the conditions of experiment, but also at a much lower temperature in the neighbourhood of 250°.

A study of the characteristics of this first stage of inflammation has shown that the minimum temperature necessary to cause the appearance of the cold flame, like that of the true flame, diminishes slowly on ascending the homologous series. The violence of the explosion and the size of the flame also increase with the length of the carbon chain of the fuel. The presence of a double bond or an alcohol or acid group in the open-chain compound lowers the oxidation tendency of the mixture, and the spontaneous ignition temperature is then in the neighbourhood of 250° C.; the presence of aldehyde or ether groups increases noticeably this tendency, as also does the addition to the mixture of small quantities of an alkyl hydrogen peroxide. A saturated or monoethylenic cyclic hydrocarbon is also readily oxidized, but on the contrary the benzene derivatives are not rapidly oxidized, and do not ignite at lower temperatures than 300° C. at atmospheric pressure; neither do ethane, methane, nor ethylene and propylene. In all these cases the oxidation reactions are accelerated by increasing the concentration of the combustible constituent of the mixture. A more or less large excess of hydrocarbon is necessary to cause spontaneous ignition at 250° C. at 1 atm. pressure.

(*b*) **Ignition at Increased Pressures.** All recent determinations at pressures higher than atmospheric give ignition temperatures lower than, or equal to, 300° C. This is shown by the results of Tizard and Pye [46, 1922, 1926], of Lewis [23, 1930], Dumanois [12, 1928], Mondain-Monval [28, 1929–30], and Quanquin [38, 1931], and especially by the very complete results of Townend and his collaborators [47, 1934]. The latter investigator studied the effects of increased pressure between 0·75–10 atm. on the ignition temperature of various hydrocarbons, especially pentane and hexane. In contrast to the results summarized above they did not obtain a true flame at 300° C. with certain mixtures of air and pentane at atmospheric pressure. Only hexane air mixtures containing more than 5% hexane ignited below 300° C. at 1 atm. pressure in their experiments. Mixtures containing less combustible material required pressures of 1·25–1·75 atm. for ignition to take place at lower temperatures. In the case of pentane air mixtures the phenomena observed with hexane set in at 0·25 atm. pressure above the atmospheric pressure; this divergence from the preceding results (of Prettre) can perhaps be explained by the differences in the experimental methods used.

The principal result, however, of Townend's work is to show that the two ignition temperature zones discovered by Prettre under certain experimental conditions do not both exist at all pressures, but that at sufficiently high pressures ignition should occur at all temperatures above 250° C. In agreement with what all the investigators mentioned have found, Townend confirmed that the minimum pressure necessary for ignition at 300° C. diminished as the molecular weight of the hydrocarbon increased, and therefore the oxidizability and the inflammability between 200 and 300° C. of these substances is a function of this molecular weight. Townend also noted that with isomers it was always those with unbranched straight chains which were most easily oxidized and ignited at about 300° C.

It can therefore be concluded that all the measurements made on oxidation and ignition between 200 and 300° C. of paraffinic hydrocarbons which are the constituents of normal petrols result in placing these compounds in a class together.

Comparison of the Results with the Resistance of Fuels to Knock.

Campbell, Lovell, and Boyd [7, 1928] examined in a test engine the influence of the concentration of the fuel on knocking. They proved that a deficiency of air increased the knock tendency and its violence. However, it has just been mentioned that a deficiency of air increases the oxidation velocity and susceptibility to ignition, and tends to lower the minimum ignition temperature to about 250° C. and to diminish the ignition delay.

The same authors [24, 1931, 1933–4] measured the resistance to knock of a large number of saturated olefinic and acetylenic hydrocarbons of the fatty and aromatic series. In order to determine this they found the aniline equivalent of each mixture, that is, the number of centigram molecules of aniline added to or taken from a litre of reference spirit, needed to increase resistance to knocking to the same extent as by the addition to the reference spirit of one molecule of the substances under examination. The following table shows that the classification obtained is substantially similar for different workers who have systematically studied the slow oxidation or ignition of hydrocarbons between 200 and 300° C.

The table proves that the knock tendency, or oxidation and ignition, are effected by the following factors: pressure, concentration, and particularly the constitution of the combustible mixture. In every case an increase of molecular weight increases the knock tendency provided the carbon chain is not modified. The presence of a double bond or numerous branches in the chain, e.g. CH_3 groups, diminishes the oxidation tendency and increases the aniline equivalent. The benzene hydrocarbons are the least readily oxidized and are about the most resistant to knocking.

It is not important that there are differences between the various numerical results obtained by different authors on the same substance, since the apparatus used was different and various secondary factors modify more or less the oxidation reactions. Amongst these secondary factors should be mentioned hot cylinder walls, the ratio of surface to volume of the vessel, the time of contact of the gas with the hot surface at the reaction temperature, and the duration of the preliminary heating period.

Very different numerical results have been obtained when the aniline equivalent has been measured on different engines, but the general classification of the hydrocarbons as regards oxidation has not been appreciably changed. This is not the case for those petrols which can be classed in a different order according to the apparatus in which the tests are made. The petrols are always a complex mixture of hydrocarbons, and each has its own susceptibility to oxidation; those least readily oxidized can under certain conditions act as inhibitors to the oxidation of the other constituents; even a small modification of these conditions is sufficient to suppress this inhibitory action.

It must therefore be concluded that the resistance to knock of a combustible mixture depends mainly on its chemical constitution, and that this resistance is directly related to its oxidizability. A study of the action of anti-knocks on slow and explosive combustion confirms this point of view.

Action of Anti-knocks.

Anti-knocks, such as lead tetraethyl (Midgeley [27, 1923]), diminish the knock tendency of hydrocarbons; their range is limited, in that it is not possible, by the addition of large amounts of anti-knocks, to increase the octane number of a very bad spirit to a high level (Heble, Rendel, and Garton [20, 1933], Campbell, Signaigo, Lovell, and Boyd [8, 1935]).

Many experiments have been carried out in order to confirm the hypothesis that knocking is caused by a modification of the flame region caused by the igniting spark; a modification which implies the formation of an explosion wave. According to this theory, anti-knocks would render the production of detonation more difficult by diminishing the velocity. Experience has shown that neither the commencement of the explosion wave nor its velocity was modified by the addition of lead tetraethyl to the mixture (Egerton and Gates [16, 1927], Laffitte and Dumanois [21, 1928]). In contrast all anti-knocks, even the less efficient, have a large effect on the oxidation ignition reactions; all experiments are in accord on this point. Moureu, Dufraisse, and Chaux [30, 1927], also Callendar [6, 1927] and Egerton and Gates [16, 1927], have shown that the velocity of absorption of oxygen by petrol and paraffin was greatly retarded by lead tetraethyl, and various other anti-knocks. Lewis [23, 1927, 1929–30], Dumanois and Mondain-Monval [12, 1928], Mondain-Monval [28, 1929–30; 29, 1933, 1935], Quanquin [38, 1931], observed that progressive heating of hydrocarbon mixtures in closed vessels, which would normally cause explosive reactions between 220 and 250° C. in the absence of anti-knocks, did not cause ignition of these mixtures even at 300° C. when a little lead tetraethyl was added, slow oxidation itself becoming negligible. Ignition at 250° C. under atmospheric pressure is suppressed by the addition of small quantities of anti-knocks. The addition of 10% of benzene to pentane had the same effect, but then the cold flame subsisted between 250 and 350° C. In the presence of lead tetraethyl, the cold flame was not visible below 350° C., and in all these cases the spontaneous ignition temperature was higher than 600° C. (Prettre [35, 1932]).

On rapidly heating mixtures by adiabatic compression these ignited under increased pressure at similar temperatures whether they did or did not contain lead tetraethyl, Pignot [33, 1926]. This would appear to contradict the observations of Lewis and of Mondain-Monval.

An explanation of this divergence has been given by Townend and his collaborators [47, 1934], who have shown that the effect of anti-knocks is to displace towards high pressures the curve expressing the ignition temperature as a function of the pressure. Thus when an anti-knock has considerable influence at ordinary pressure, the ignition temperature being raised more than 150° C., it has no effect at high pressures. The effective range of anti-knocks can be extended towards high pressures, under different experimental conditions from those of Townend (for example under those of Mondain-Monval), but it would always be limited, thus explaining the results obtained in engine tests.

Intermediate Oxidation Products between 200 and 300° C.

Apart from carbon monoxide, hydrogen, carbon dioxide, and water vapour, the partial oxidation products of the paraffin hydrocarbons, as found by the various experimenters, are: ethylenic hydrocarbons, or saturated carbon chain compounds shorter than the initial hydrocarbon, aldehydes, and peroxides. In particular Quanquin [38, 1931] has indicated that the partial oxidation products of hexane contain the following peroxides CH_3OOCH_2OH; $C_2H_5OOCH_2OH$; and the work admitted the existence of the compound CH_3OOH. The characteristic reactions of organic peroxides have been obtained by numerous authors in the analysis of the products, at the beginning stages of combustion and under very different experimental conditions.

The great instability of alkyl peroxides at temperatures above normal shows that only a very small fraction of these substances can escape practically instantaneous decomposition at temperatures of 200–300° C., especially at ordinary pressures. Experimenters have tested only a very small fraction of the peroxidic substances that give slow combustion, yet they have detected quite appreciable quantities. This is the proof of the importance of the peroxidation reactions which are a necessary intermediate stage in slow and explosive combustion between 200 and 300° C.

The numerous researches of Bone and collaborators [4, *Influence of the Carburant on Oxidation, Ignition, and Aniline Equivalent*

	Temperatures at which oxidation commences			*Temperatures at which cold flame appears (Prettre)*	*Minimum ignition temperatures*														*Aniline Equivalent*
	T.I.C. of Callendar	*C.I.T. of Lewis*	*T.T.R. of Mlle Estradère*		*Prettre*	*Lewis*	*Dumanois, Mondain-Monval, & Quanquin*	*Tizard & Pye*	*Townend, Cohen, & Mandlekar*										
Pressures (atm.)	1	2	1	1	1	2	10	..	..	0·75	1	1·25	1·5	1·75	2	3·25	5	10	..
Heating velocity	..	slow	rapid	rapid	rapid	slow	slow	adiabatic compression	very rapid										in an engine
									% of carbon										
Hydrocarbons:									..	..	..	..	..	..	..	..	..	..	..
Propane	..	..	..	225–70	304	..	..	..	3	..	570	..	..	460	*340*	..	..	300	..
n-Butane	..	..	..	..	..	..	..	..	8	..	560	..	..	*340*	325	..	..	310	..
									3	..	590	..	..	..	..	480	*350*	325	..
Isobutane	..	..	..	..	..	..	..	..	8	..	540	..	..	..	..	*350*	325	320	..
									2·4	..	548	535	..	*338*	..	..	288	..	+1
n-Pentane	295	255	..	225–42	259–63	255–7	229–37	..	7·4	..	510	*338*	..	300	..	..	285	..	..
									2	610	570	..	510	..	*295*	..	..	275	−6
n-Hexane	265	230	330	220–30	253–6	232–3	222–32	300–6	4	560	525	..	*275*	..	270	..	..	265	..
									6	540	*285*	..	280	..	275	..	..	265	..
n-Heptane	..	209	300	210–30	252–8	218–20	219–30	280–5	.	..	..	..	..	..	..	..	..	..	−14
n-Octane	..	197	..	200–15	245–52	203–4	215–26	275–80	..	..	..	..	..	..	..	..	..	..	−21
n-Nonane	205	193	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	−28
Isooctane	..	..	500	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	+16
Pentene	..	240	..	260–70	300–05	241–2	..	..	..	..	..	..	..	..	..	..	..	..	+10
Cyclohexane	..	..	345	235–60	261–3	..	..	..	..	..	..	..	..	..	..	..	..	..	+7
Cyclohexene	..	..	410	255–60	273–5	..	..	..	..	..	..	..	..	..	..	..	..	..	+10
Benzene	670	..	650	670	695	..	..	..	..	..	..	..	..	..	..	..	..	..	+10
Toluene	550	.	..	600	685	..	..	..	..	..	..	..	..	..	..	..	..	..	+15

1927, 1929] have led this investigator to affirm frequently that he had never established the presence of peroxides. But the work of Bone has never been carried out on hydrocarbons capable of oxidation and ignition in the range 200–300° C.; they have been limited to gases such as methane, ethane, and ethylene; none of these are oxidized to any pronounced extent below 300–400° C. Experimenters who have detected the presence of peroxides have not worked with these gaseous hydrocarbons. There is therefore no contradiction between the statements made by Bone and the certain presence of peroxides in the oxidation of long-chain carbon compounds. Bone's results are not an obstacle in the way to conclude that the principal constituents of petrol oxidize and ignite according to processes which include the intermediary formation of alkyl peroxides. The abundant formation of peroxides in I.C. engines has been demonstrated by the experiments of Dumanois, Mondain-Monval, and Quanquin [13, 1931]. The knowledge of the energy of intra-atomic linkages makes it more probable that peroxide molecules should be formed at fairly low temperatures than any other product of oxidation which demands the preliminary formation of atoms from the molecule of oxygen. The formation of atomic oxygen requires 117,000 g.-cals., whereas the energy necessary to break down a paraffinic carbon chain never exceeds 70,000 g.-cals., and this energy diminishes for the linkages between the central carbon atoms when the chain is lengthy. There is therefore an evident parallelism with the oxidizability. This is confirmed by the higher value corresponding to the binding of the carbon atoms in the benzene nucleus, which is oxidized only with difficulty, and does not easily cause knocking.

The analytical results do not, however, permit the successive oxidation reaction stages to be completely given. The primary oxidation product may be of the type $R—CH_2—O—O—CH_2—R$, but has never been isolated from the paraffin hydrocarbons. Nevertheless, the investigations of Rieche [41, 1931] and his collaborators, on the dissociation of peroxides and the reactions of these compounds with aldehydes, provide an explanation of the transformation of the primary product, again hypothetical, into peroxides of lower molecular weight, such as have been mentioned. A reasonable but nevertheless uncertain scheme of the successive stages of oxidation can be established by using these results.

Together with peroxides, ethylenic hydrocarbons with molecular weights less than the initial products have been frequently isolated. It is certain that during oxidation free radicals are formed in a transitory state, and these lead to the formation of various hydrocarbons such as methane, ethane, and ethylene. Rice [40, 1934] has stated that the tendency of the paraffins to cause knocking increases with their tendency to dissociate into free radicals in the absence of oxygen, or when oxygen is in defect. These free radicals which, as well as hydrogen and oxygen atoms, can cause dissociation of hydrocarbons, of the peroxides, and of other intermediary products, are very reactive; they accelerate oxidation considerably, giving rise to chain reactions. According to Norrish [31, 1935] similar reactions occur with methane, ethane, and ethylene; these will not be discussed in this article.

A study of the absorption spectra of hydrocarbon mixtures in the course of oxidation has seldom been attempted; it has, however, already furnished information of great importance. Egerton and Pidgeon [17, 1933] have examined in this way the slow combustion of butane, and have proved that during the induction period absorption bands characteristic of aldehydes, fatty acids, and peroxides were present together with a band in the neighbourhood of 2,600 A., corresponding to a radical or compound not yet identified. The concentration of this latter compound diminishes rapidly as aldehyde, fatty acid and peroxide increase. These results are sufficient to show the value of this method of measurement. These experiments must be compared with those of Withrow and Rassweiler [51, 1933–4], carried out on an engine. Spectrographs have shown that hydrocarbon mixtures not yet reached by the flame from the igniting spark show the absorption bands of aldehydes even when the engine was not knocking; this proves that a definite and very rapid oxidation takes place in the engine. The addition of lead tetraethyl suppresses knocking but the aldehyde concentration remains constant; however with aniline, a less effective anti-knock, there is a diminution of the aldehyde formation, thus indicating that these two anti-knocks do not act on the same stage of the oxidation reactions.

The Velocity and Mechanism of the Oxidation Reaction between 200° C. and 300° C.

In order that the oxidation phenomena can play a part in engines where the hydrocarbon mixtures only remain for a very short time, it must be realized that under the conditions of temperature and pressure in an engine giving rise to knocking the oxidation velocity is considerable. This has been qualitatively proved by the work of Dumanois, Mondain-Monval, and Quanquin and of Withrow and Boyd. It is, however, a study of the kinetics of the oxidation reactions of the paraffin hydrocarbons which gives exact information on the influence of various factors, such as pressure, temperature, and concentration, on the velocity of combustion leading to ignition. These studies have been but rarely undertaken with liquid hydrocarbons; indeed, the researches of Pidgeon and Egerton [32, 1932] are the only ones which are nearly complete on the subject that have been published up to the present. These authors have examined mixtures of pentane and oxygen at temperatures below 300° C.

The effect of pressure on the oxidation velocity is considerable, the reaction apparently being of the third order. Inert gases such as nitrogen accelerate the reaction, and an increase in the concentration of the pentane similarly acts in the same direction only more pronouncedly; an increase of the hot surfaces of contact, on the contrary, has an inhibitory effect. The induction period which precedes the slow oxidation, and at higher temperatures the ignition-point, is still more sensitive to these different accelerating influences.

Under certain conditions of concentration and state of walls, it is possible to show the very pronounced effect of pressure on hydrocarbon mixtures, especially of the more readily oxidized combustibles. The apparent order is then often greater than 5; that is the velocity V, of the reaction examined, varies more rapidly with the pressure than would be given by the expression $V = K.p^5$, Prettre [36].

The considerable influence of various factors, such as pressure concentration, surface, and especially that of inert gases, proves beyond doubt that oxidation reactions depend on 'chain mechanisms', the theory of which has been formulated by Semenoff [42, 1935]. It should simply be recalled here that a general characteristic of chain reactions is that they are always accelerated very considerably by pressure and by the presence of inert gases (such as nitrogen from the air in the case of I.C. engines).

The induction period which precedes ignition is considerable at ordinary pressures—from 10 to 15 sec. at least, but the pressure should act greatly on the oxidation reactions which happen during this period. Its action on the rate is about the fourth, or fifth, power if the reactions are produced isothermally. This is, however, not the case, for the cold flames preceding ignition are accompanied by considerable exothermic phenomena. To the effect of pressure is added that of temperature, so that the rate can be much greater than that given by the classical kinetics, for the temperature coefficient is high (3-4 times for 10° C.), and the 'apparent order' of reaction often increases with the temperature in chain reactions. Townend, Cohen, and Mandlekar [47, 1934] examined the effect of pressure and temperature on the reaction velocity leading to ignition and, under the chosen experimental conditions, extrapolation of their figures for the delay of ignition has shown that at 390° C. the delay necessary to cause thermal explosions becomes less than 0·005 sec. when the pressure was greater than 4 atm. Therefore it is easily seen that, during the brief time the mixtures are in the engine, oxidation is produced at a considerable velocity, which is a function of the pressure, and in some measure a function of the temperature; the logical consequence being that for such mixtures a maximum pressure cannot be exceeded without causing spontaneous ignition with a given delay, even if only a brief one.

The heterogeneity of the temperature of the combustible charge in the cylinder cannot play a sufficiently important role to prevent ignition; it has been proved that this heterogeneity cannot oppose itself to an important slow oxidation. The relatively cold walls exercise a deactivating effect, a little more pronounced than in the laboratory experiments, and the turbulence introducing into the hot gases much colder molecules only produces a slight supplementary deactivation. All these effects are easily compensated for by a slightly increased pressure, and the spontaneous ignition with only slight delay will need only slightly greater pressure because of the high order of the reactions in spite of the effect of the cold walls and the turbulence.

Heterogeneity of temperature caused by turbulence exists apart from the heating of the gas due to adiabatic compression by the piston. This latter diminishes rapidly when the slow oxidation becomes so great that its thermal effects exceed the effect of compression. It is therefore useless to attempt to calculate the temperature of mixtures injected into a cylinder by the aid of measurements of pressure.

The Spontaneous Ignition Flame Velocity.

All experimenters would agree that spontaneous ignition of a combustible mixture when exposed at all points to a nearly uniform temperature is characterized by the simultaneous appearance and disappearance of the flame throughout the gas. Tauzin [44] has attempted to record the flame velocity due to ignition of a mixture of $2H_2+O_2$. The apparatus used enabled him to detect propagation velocities up to 1,000 metres per sec., but in spite of this sensitivity he was unable to record any movement of flame, either from the centre of the gas to the walls, or vice versa. The formation of the detonation type of combustion would not be expected from the conditions of temperature and pressure in his experiments. It must therefore be concluded that the explosive reaction was simultaneous at all points of the mixture examined: the duration of the luminous phenomena did not exceed 0·01 sec. The explosion resulting from the ignition is therefore simultaneous at all points of the mixture and lasts a very short time. Consequently this suffices to explain the formation of a shock wave which is sufficient to explain the violence of the effects due to such ignitions, since they are produced at a high pressure. The mechanical effects of knocking observed in engines are therefore easily explained without referring to a detonation wave, of which the mechanical effects would be far greater.

The results of Tauzin seem to be completely comparable with the photographic record of Withrow and Boyd [50, 1931] on the movement of flame in engines giving rise to knocking, as are also the results obtained by Duchene [10, 1932].

If large differences of temperature, pressure, and concentration exist in the combustible mixture in a cylinder, then ignition would certainly occur first at a point particularly favoured by these factors which cause rapid oxidation. This fact was observed by Withrow and Boyd on certain of their photographs. This heterogeneity consequently can cause ignition to occur successively at various points in the mixture. The photographic record will then register the movement of flame, the velocity of which would be an inverse function of the retardation of ignition at various points in the mixture. There is nothing to oppose the velocity being nearly as rapid as a detonation. But it will never become a true explosion wave. It is the explosive capacity of the initial mixture which principally governs the conditions for the formation of the detonating type of combustion. Dilution with large amounts of inert gas (e.g. nitrogen from the air) prevents so rapid a flame; an increase in pressure certainly acts in the opposite manner, but at 10 atm. a theoretical mixture of pentane and air does not detonate at ordinary temperatures (Egerton and Gates [16, 1927]). In I.C. engines the pressure reaches between 20 and 25 atm. at the moment when knocking occurs, but the absolute temperature of the gas is at least doubled at this moment, due to adiabatic compression, and the resulting thermal expansion reduces the efficacy of this pressure.

The results obtained by Egerton and Gates are therefore probably applicable to most engines.

Slow oxidation can never facilitate formation of a detonation wave. If more explosive substances than the initial hydrocarbon mixtures be formed in the presence of oxygen, such as peroxides for example, there are formed at the same time compounds which cause practically no detonation, such as the lower molecular weight hydrocarbons, and carbon monoxide, or completely inert substances such as carbon dioxide and water vapour. At the same time the oxygen concentration greatly diminishes. This explains why, whatever the initial pressure, no experiment on the formation of the detonation wave has yet shown that the temperature necessary to cause oxidation of the usual hydrocarbon air mixture facilitates the formation of this wave.

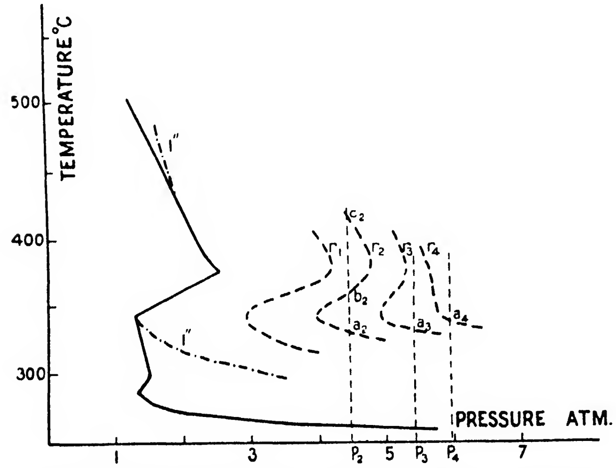
A theory has been put forward that the radiations from the flame due to ignition would be capable of causing detonation by modifying photochemically the mixture at the farther end of the combustion chamber and causing it to detonate. Attempts to verify this theory have been made, by submitting a portion of a mixture to a very intense luminous flux—they have been without result. Paraffin hydrocarbons are absolutely inert to visible radiations, and to the near ultra-violet radiation: oxygen is only changed photochemically in the Schumann region, equal or less than 1,750 A. Such experiments can only be conclusive with wave-lengths capable of modifying the initial mixture: the extreme end of the ultra-violet, which certainly gives atomic oxygen or perhaps the infra-red.

Oxidation and Ignition at Temperatures above 300° C.

At atmospheric pressure mixtures of air and hydrocarbon vapours no longer ignite above 300° C.: the slow oxidation velocity then falls to a lower value than at about 250° C. (Prettre [36]). The curve of the ignition temperature as a function of the pressure shows that the minimum pressure necessary to cause ignition increases to several atmospheres when the temperature is raised to between 350° C. and 400° C. (Townend [47, 1934]). Above 400° C. the temperature again has its usual favourable influence on oxidation and ignition.

The abrupt diminution of oxidation between 300° C. and 400° C. imposes an important modification on the chain of reactions. The peroxides are in effect no longer detectable at these temperatures, however short the contact of the mixture with the hot surface. The investigations of Bone [4, 1927, 1929] have been carried out mainly on oxidation at temperatures equal to or greater than 400° C.: his conclusions are therefore perfectly applicable to those temperatures. The recent investigations of Norrish [31, 1935], Thompson and Hinshelwood [45, 1929] have shown that these combustions as with those produced at much lower temperatures are dependent on chain reactions.

The problem arises whether this slowing down of the rate of oxidation between 300° C. and 400° C. can influence the spontaneous combustion phenomena in engines. The measurements of Townend, Cohen, and Mandlekar [47, 1934] on the delay of ignition at different temperatures and pressures furnish valuable indications on this subject. In the pressure-temperature curves (see graph), the ignition temperatures of a hydrocarbon mixture obtained by Townend are plotted as a continuous line, and the curve showing the minimum pressure necessary to produce ignition at various temperatures, after a delay of 1 sec. in each case, are plotted thus: —·—·—·—. The path of this latter curve implies that it would be similar for much shorter delay periods r_1, r_2, r_3, curves shown thus: — — —. At about 300° C.–350° C. there is, as indicated by Townend, a particular temperature interval, for which the delay is smaller at a given pressure than that involving a higher or lower temperature. Thus in an engine in which a mixture remains in the cylinder for a length of time greater than the delay r_2, then ignition occurs when a temperature given by the point a_2 is reached: but if the velocity of heating is much greater, then the temperature b_2 would be attained in a time less than r_2, and hence a temperature c_2 must be reached in order to obtain ignition; if the mixture does not attain this temperature then ignition will not take place. At higher pressures the zone a_2b_2 is more extended, and it would be difficult to exceed it without causing ignition. At the same time, the ignition delay between 300° C.–350° C. diminishes and the curve of short delays cannot have any more opposing slopes, curve r_4. It is therefore useless to have high engine temperatures, as oxidation and ignition then are set up nearly instantaneously. Anti-knocks, since they displace the curve of ignition temperatures towards higher pressures, act the same on the curves of equal ignition delay.



The influence of pressure on the spontaneous ignition temperature and on the retardation of ignition of mixtures of air and paraffinic hydrocarbons.

Injection Engine Fuels.

As for petrols these fuels possess an oxidizability and an inflammability directly connected with their chemical constitution. Paraffinic and cyclic molecules, when they are slightly branched or unbranched, would give rise to ignition more readily; fuels possessing the benzene type of structure would be less readily oxidized and ignited. Measurements on the efficacy of these types of fuel and the establishment of a scale of cetane numbers, using mixtures of cetane and mesitylene (Boerlage and Broeze [3, 1931]) have confirmed this point of view. An analogy between injection-engine fuels and their aptitude in causing knocking in I.C. engines has been shown by Dumanois [11, 1933]. This again shows the relation between knocking and oxidation and ignition phenomena.

Conclusion.

The sensitiveness to knock of a fuel and its behaviour on ignition in an I.C. engine are closely related to its susceptibility to oxidation and to spontaneous ignition; on the contrary the rapidity with which the detonation wave is formed is not connected with knocking or explosibility. The influence of anti-knocks in engines can only be explained by their inhibitory action on the thermal combustion.

Although the results already obtained are sufficient to establish certain conclusions, our knowledge of the actual changes occurring in a mixture under engine conditions is still very incomplete. It is known that various bodies such as peroxides and aldehydes are formed, and the presence of free radicals and atoms can be affirmed. It has been proved that the reactions have a chain mechanism, but there is some way to go yet before a quantitative representation can be given of the importance and of the velocity of the various elementary processes which comprise such complex oxidations.

The practical interest of these combustions and their theoretical importance to chemical kinetics demand and allow hope of further investigations in this field.

REFERENCES

1. Berl, E., Heise, K., and Winnacker, K. *Z. phys. Chem.* **139,** 353 (1).
2. Bodenstein, M. *Z. phys. Chem.* **12** B, 151 (1931); *Z. Elektroch.* **38,** 911 (1932).
3. Boerlage, G. D., and Broeze, J. J. *Engineering*, 603, 687, 755 (1931).
4. Bone, W. A., and Townend, D. T. A. *Flame and Combustion in Gases* (London, 1927); Bone, W. A., Hewitt, D. M., and Townend, D. T. A., *Gaseous Combustion at High Pressures* (London, 1929). Bone, W. A., and Hill, S. G., *Proc. Roy. Soc.* **129** A, 434 (1930). Bone, W. A., and Allum, R. E., *Proc. Roy. Soc.*, **134** A, 578 (1932). Bone, W. A., and Haffner, A. E., and Rance, H. F. *Proc. Roy. Soc.*, **143** A, 16 (1933). Bone, W. A., and Lamont, F. G., *Proc. Roy. Soc.*, **144** A, 250 (1934).
5. Brunner, M., and Rideal, E. K. *J.C.S.* 1162 and 2824 (1928).
6. Callendar, H. L. *Engineering*, 121 (1927).
7. Campbell, J. M., Lovell, W. G., and Boyd, T. A. *Ind. Eng. Chem.* **20,** 1045 (1928).
8. Campbell, J. M., Signaigo, F. K., Lovell, W. G., and Boyd, T. A. *Ind. Eng. Chem.* **27,** 593 (1935).
9. Dixon, H. B. *Rep. Imp. Motor Transport Conf.* (1920).
10. Duchene, R. Publ. Tech. Minis. Air, no. 11, 1 vol. (1932).
11. Dumanois, P. *Compt. rend.* **196,** 1003 (1933).
12. Dumanois, P., and Mondain-Monval, P. *Compt. rend.* **187,** 892 (1928); *Ann. Comb. Liq.* **3,** 761 (1928).
13. Dumanois, P., Mondain-Monval, P., and Quanquin, B. *Compt. rend.* **192,** 486 (1931).
14. Edgar, G. *Ind. Eng. Chem.* **19,** 145 (1927).
15. Egerton, A. C., and Gates, S. F. *J.I.P.T.* **13,** 244, 256, 273, 281 (1927); **14,** 656 (1928).
16. Egerton, A. C., and Gates, S. F. *Proc. Roy. Soc.* **114** A, 149 (1927).
17. Egerton, A. C., and Pidgeon, L. M. *Proc. Roy. Soc.* **142** A, 26 (1933).
18. Estradère, S., Mlle. Publ. Tech. Minis. Air, no. 49, 1 vol. (Paris, 1934).
19. Fort, R., and Hinshelwood, C. N. *Proc. Roy. Soc.* **127** A, 218; **129** A, 284 (1930).
20. Hebl, L. E., Rendel, T. B., and Garton, F. L. *Ind. Eng. Chem.* **25,** 187 (1933).
21. Laffitte, P. See Article 9.
22. Laffitte, P., and Dumanois, P. *Compt. rend.* **186,** 146 (1928).
23. Lewis, J. S. *J.C.S.* 1555 (1927); 759 (1929); 58 and 2241 (1930).
24. Lovell, W. G., Campbell, J. M., and Boyd, T. A. *Ind. Eng. Chem.* **23,** 26, 555 (1931); **25,** 1107 (1933); **26,** 475 (1934).
25. Mardles, E. W. *J.C.S.* 873 and 3155 (1928); *Trans. Faraday Soc.* **24,** 574 (1928); **27,** 681 (1931); **28,** 69 (1932).
26. Mason, W., and Wheeler, R. V. *J.C.S.* **121,** 2079 (1922); **125,** 18 (1924).
27. Midgeley, Jr. T. *Ind. Eng. Chem.* **15,** 421 (1923).
28. Mondain-Monval, P., and Quanquin, B. *Compt. rend.* **189,** 917 (1929); **191,** 299 (1930).
29. Mondain-Monval, P., and Wellard, R. *Compt. rend.* **196,** 1226 (1933); **200,** 232 (1935).
30. Moureu, C., Dufraisse, C., and Chaux, R. *Chim. et Ind.* **17,** 531 (1934); *Chim. et Ind.* **18,** 3 (1927); *Compt. rend.*
31. Norrish, R. G. W. *Proc. Roy. Soc.* **150** A, 36 (1935).
32. Pidgeon, L. M., and Egerton, A. C. *J.C.S.* 661, 676 (1932).
33. Pignot, A. *Compt. rend.* **182,** 376 (1926); thesis (Paris, 1926).
34. Pope, J. C., Dykstra, F. J., and Edgar, G. *J.A.C.S.* **51,** 1875, 2203 and 2213 (1929).
35. Prettre, M. *Ann. Comb. Liq.* **6,** 7, 269, 533 (1931); **7,** 699 (1932).
36. —— Unpublished results.
37. Prettre, M., Dumanois, P., and Laffitte, P. *Compt. rend.* **191,** 329 and 414 (1930).
38. Quanquin, B. Thesis (Paris, 1931).
39. Ricardo, H. R. *Inst. Aut. Eng. Rept. Emp. Mot. Fuels*, **18,** **1,** (1923).
40. Rice, F. O. *Ind. Eng. Chem.* **26,** 259 (1934).
41. Rieche, A. See *Alkylperoxyde und Ozonide*, 1 vol. (Dresden, 1931).
42. Semenoff, N. See *Chemical Kinetics and Chain Reactions*, 1 vol. (Oxford, 1935).
43. Spence, R. *J.C.S.* 686 (1932); *J.A.C.S.* **52,** 1162, 2824 (1928).
44. Tauzin, P. Unpublished results, communicated to the author.
45. Thompson, H. W., and Hinshelwood, C. N. *Proc. Roy. Soc.* **125** A, 277 (1929).
46. Tizard, H. T., and Pye, D. R. *Phil. Mag.* (vi), **44,** 79 (1922); (vii) **1,** 1094 (1926).
47. Townend, D. T. A., Cohen, L. L., and Mandlekar, M. R. *Proc. Roy. Soc.* **146** A, 168 (1934).
48. Wellard, R. Thesis (Paris, 1935).
49. Wheeler, R. V. *J.C.S.* **113,** 840 (1918); **121,** 2079 (1922).
   Wheeler, R. V., and Blair, E. W. *J.C.S.I.* **41,** 303 T (1922).
50. Withrow, L., and Boyd, T. A. *Ind. Eng. Chem.* **23,** 539 (1931).
51. Withrow, L., and Rassweiler, G. M. *Ind. Eng. Chem.* 25, 1359 (1933); **26,** 1256 (1934).

IGNITION

5. IGNITION IN GASES WITH SPECIAL REFERENCE TO KNOCK PROBLEMS

By D. M. NEWITT, D.Sc., and D. T. A. TOWNEND, D.Sc.
Imperial College of Science and Technology

Introduction

THE ignition of an explosive gaseous medium may be effected by a number of means, as, for example, by an electric spark, contact with a hot element, flame, or other external source of heat, or it may occur spontaneously if its temperature and/or pressure be sufficiently raised, as by adiabatic compression, so that self-heating of the medium as a whole is induced. It is to the last-named category that we propose in this article to restrict our consideration of ignition, for it is now generally recognized that the behaviour of any fuel in an engine is largely influenced by the chemical reactivity of the unburnt medium ahead of the flame as controlled by the degree of compression, the working temperature, and speed of running. In such circumstances, where the available time interval is very short, any *appreciable* chemical reaction must *ipso facto* be intense and conditions will proximate closely to those of the ignition point; indeed, since the work of H. T. Tizard and D. R. Pye [42, 1922], to which we shall refer in more detail, it has been accepted that in general there is a close relationship between both the chemical reactivity and spontaneous ignition temperature of a fuel and its knocking propensity in an engine.

The measurement of 'ignition temperatures' is therefore a matter of great interest in gaining some insight into the probable behaviour of fuels in an engine. As will be seen in what follows, however, the subject as a whole is far more complex than has hitherto been supposed, and great care has to be exercised in drawing any inference from individual data without taking into full consideration all the special experimental circumstances under which they have been determined. Before dealing with some of the experimental results for ignition temperatures of fuels and their relationship with engine problems, it may be of advantage briefly to consider the theoretical aspect of the subject generally.

Pre-flame Combustion. Chemical change may be determined in a gaseous explosive mixture at a much lower temperature than is required to develop flame; in such circumstances, however, the rate of combustion is slow. With rise of temperature the reaction becomes more rapid, an increase of some 10° C. usually resulting in a speeding up of the reaction of from 2 to 4 times.

According to the classical view of Arrhenius there exists in a gaseous system an equilibrium between 'normal' and 'active' molecules (k = [active form]/[normal form]), the latter alone being capable of participating in chemical reaction. 'Active' molecules were supposed to be formed endothermically from 'normal' molecules, so that with rise in temperature the shift in equilibrium towards an increase in the concentration of 'active' molecules would be governed by the van't Hoff equation

$$\frac{d\log k}{dT} = \frac{E}{RT^2}$$

E being the heat absorbed in activating a normal molecule. The reaction rate, k, being dependent upon the number of active molecules which was considered small in proportion to the number of normal molecules, the above equation on integration yielded

$$k = Ce^{-E/RT}.$$

On these premises an ignition temperature has hitherto been defined as that temperature to which an explosive medium must be raised so that the heat lost from the system by conduction through the walls of the enclosure is more than counterbalanced by the rate at which it is evolved by the interaction; the reaction thus becomes self-accelerating, the temperature rising until ignition occurs and flame appears.

It will be clear, therefore, that an ignition temperature does not necessarily correspond with an instantaneous appearance of flame; indeed, there is invariably a definite 'pre-flame period' or 'lag' during which combustion is self-propellant. The duration of such lags may vary between a small fraction of a second and 2 hours or even more depending upon the experimental conditions, a consideration of paramount importance in evaluating an 'ignition temperature' in so far as it may have any bearing on conditions prevailing in internal-combustion engines; for in such circumstances an ignition temperature would have little significance unless the corresponding lag were of the order of, say, 0·005 sec.

During the past decade a new outlook has arisen in regard to the factors controlling the velocities of exothermic chemical reactions due to the conception of 'chain reactions', a subject to which we have also referred elsewhere (Combustion Phenomena of Hydrocarbons, p. 2860). According to this more recent view, when a reaction occurs between suitably energized molecules the product(s) which possess both the heats of 'activation' and 'reaction' do not pass this on by indiscriminate collisions to the gaseous system as a whole, thereby causing general temperature rise, but by specific encounters with suitable reactant molecules hand on the energy to them quantumwise. In this way the progress of general chemical reaction is related to the number, length, and multiplication of so-called 'chains'.

A chain of the type referred to is termed an 'energy' chain; frequently, however, a chemically active product (maybe a free radical) is postulated which after suitable collision is responsible for the regeneration of a 'chain carrier'. Thus, for example, in the oxidation of methane an O-atom has been postulated by R. G. W. Norrish [31, 1935] as the 'carrier' as follows:

$$CH_4+O \rightarrow :CH_2+H_2O. \qquad \text{(i)}$$

$$:CH_2+O_2 \rightarrow H{\cdot}CHO+O. \qquad \text{(ii)}$$

It is considered that chains may be either initiated or broken both on the walls of the containing vessel or in the gas phase, according to circumstances. Under suitable conditions it is thought probable that for each initial molecular reaction two 'carrier' atoms or molecules may be generated for each one taking part in the initial encounter. Thus, according to Norrish's view, in the course of the combustion of methane it is possible that the formaldehyde produced in (ii) may itself be oxidized via per-formic acid yielding formic acid and a further O-atom, thus:

$$\mathrm{H{\cdot}CHO+O_2 \rightarrow H{\cdot}COOH+O.} \qquad \text{(iii)}$$

When this occurs the process is referred to as a 'branching chain' mechanism which may give rise to an ignition.

According to the 'chain' view, the lags prior to ignition would be made up partly of (*a*) an induction period during which a surface reaction is proceeding slowly and giving rise to a requisite concentration of some material which when once reached is adequate to initiate chains through the gaseous system faster than they may be broken, and (*b*) a resultant reaction period which, should branching ensue, would give rise to ignition.

It should here be emphasized that much of the evidence for the operation of chain processes by themselves, in so far as it has been forthcoming from spontaneous ignition phenomena, relates mainly to observations at very low pressures which rarely exceed 100 mm. mercury; at higher pressures there may also be evidence of them when long lags (mainly an induction period of some minutes or more) are observed. But under the conditions of temperature and pressure corresponding with internal-combustion engines, where the time interval permissible for the development of enhanced chemical reactivity is very small, it seems probable that thermal considerations (i.e. the creation of a large number of suitably energized molecules by adequate temperature alone) play an important part.

Methods of determining Ignition Temperatures

From the foregoing it will be obvious that an ignition temperature can in no sense be regarded as a physical constant but must depend upon the experimental conditions under which it is determined. Also, it is not correct to speak of the ignition temperature of a particular combustible material but rather of that of a particular mixture of the combustible with air (oxygen). In recent years, however, it has become possible to state within a little the temperature at which a given explosive mixture will ignite spontaneously under rigidly defined conditions and after a definite time interval. It is not within the scope of this article to deal in detail with the many experimental methods which have been employed for the determination of ignition temperatures; nevertheless a few of those more commonly used may with advantage be given in outline, and attention directed to their respective drawbacks.

1. **Concentric-tube Method.** In order to obviate the part played by 'surface' which to some extent had influenced the results of earlier workers, H. B. Dixon and H. F. Coward [7, 1909] introduced their well-known 'Concentric Tube Method' in which the combustible gas and air (oxygen) were separately heated to the temperature of the enclosure before being allowed to mix. The apparatus was later improved (Dixon and Higgins [8, 1926]) so as not only to control pre-flame time lags, but also to study the influence of wide variation in gas pressure from between *c.* 50 mm. Hg to 7 atm.

As illustrating the influence of lag on the ignition points determined in a concentric-tube apparatus, attention is directed to Fig. 1, in which ignition points of ethane in air for lags between 0·6 and 10 sec. have been plotted at pressures between 100 mm. and atmospheric. Thus at atmospheric pressure, if the experimental mixture is allowed to remain in the apparatus for 10 sec., ignition can be effected at 600° C., whereas for ignition to occur in 0·6 sec. the temperature must be raised to 650° C. And the following figures show for various combustible gases or vapours at atmospheric pressure: (*a*) the minimum ignition temperatures allowing indefinite lags, and (*b*) the corresponding ignition temperatures for ignition to occur in 0·5 sec. (Coward [6, 1934]).

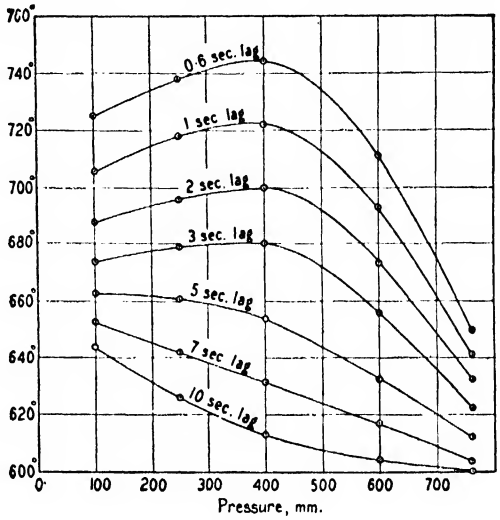


FIG. 1.

(*Reproduced by permission from 'J. Chem. Society'* (1934).)

	In air		*In* O_2			*In air*		*In* O_2	
	(*a*)	(*b*)	(*a*)	(*b*)		(*a*)	(*b*)	(*a*)	(*b*)
H_2	585	630	585	625	C_2H_4	543	627	510	604
CO	651[3]	693[1]	650[2]	687[1]	C_3H_6	..	618	..	586
		683[2]		680[2]	C_3H_8	429	435	428	..
C_2N_2	856	..	811	..	C_6H_6	..	710	..	685
CH_4	650–70	722	556–700	664	Et_2O	..	549	..	219
C_2H_6	520–630	650	520–630	628	CS_2	..	156	..	132
C_3H_8	..	..	490-570	..	H_2S	364	..	227	..
C_6H_{14}	..	600	..	355	NH_3	..	..	700–800	..

1. 0·63% H_2O in atmosphere. 2. 5·3% H_2O in atmosphere. 3. 2% H_2O in gas and atmosphere.

The concentric-tube method has also been employed recently by Dykstra and Edgar [12, 1934] in a study of the ignition of hexane-oxygen mixtures, to which we shall refer later.

The main drawback in the method is that it affords no information as to the effect of varying the proportions of combustible and air, so that presumably the results obtained thereby pertain somewhat to the most easily ignitible mixtures.

2. **Method of using a Heated Vessel.** The method of passing an explosive mixture into an evacuated vessel heated to a known temperature has been frequently employed. It originated with Mallard and Le Chatelier [24, 1880], and was used subsequently by Taffanel and Le Floch [38, 1913], Mason and Wheeler [26, 1922 et seq.], and Laffitte and Prettre [22, 1918, &c.]. It has also been used extensively in the determination of low-pressure explosion limits, and also for the determination of ignition temperatures at high pressures (Townend and co-workers [44, 1933 and 1934]). The results obtained by this method are necessarily subject to the action of the surface to which

the mixtures are exposed; moreover, although the variation of ignition temperatures with time lag is normally quite easily measurable, this becomes difficult when conditions of very short lag are under observation owing to the necessity of the small time interval required for the operation of filling. It is also necessary to guard against abnormal ignitions caused by the creation of compression waves during filling if this be too violent (cf. White [47, 1919]).

The following figures, given by Mason and Wheeler [26, 1924] for minimum ignition temperatures (indefinite lag) in a quartz vessel at atmospheric pressure, are representative of those obtained by the method:

% *methane* in air . .	3·0	5·85	7·0	8·0	9·0	10·0*	12·0	13·0
Minimum I.T. . .	700°	695	698	701	707	713	726	732
% *propane* in air . .	1·25	2·50	3·05	4·90	6·50	7·85	..	..
Minimum I.T. . .	588	552	544	525	516	514	..	..
% *butane* in air . .	1·25	2·00	2·60	3·65	4·85	7·65	..	..
Minimum I.T. . .	569	545	531	515	502	489	..	..
% *pentane* in air . .	1·5	2·15	2·75	3·75	5·30	7·65	..	..
Minimum I.T. . .	548	532	520	502	486	476	..	..

On occasion flow instead of static systems have been employed, and recently much information has been obtained thereby as to luminosity and 'cool flame' temperatures (Prettre [36, 1932]). In addition, the relative velocities of slow combustion up to the ignition point of the higher hydrocarbons have been studied over a wide range of temperatures between *c.* 200 and 600° C., notably by Pease [32, 1929 and 1934] and Edgar [35, 1929 and 1934], with results which have been very informative and to which we shall again refer (see also article Combustion Phenomena of Hydrocarbons, p. 2860).

3. **Oil-drop Method.** Most of the experimental work carried out on the higher hydrocarbons has been by the method in which a drop of the liquid fuel under tests is allowed to fall into a cup heated to a known temperature and through which a stream of air or oxygen is passing. This method, which was devised by Holm [19, 1913], is very convenient where high boiling-point fuels are under test, for they could only be handled in the vapour phase with difficulty, and at temperatures at which they would readily oxidize and/or polymerize. It provides, therefore, the only method at present available for working with Diesel fuels, the principal researches on which have been associated with the names of Holm [19, 1913], Constam and Schlaepfer [5, 1914], Wollers and Emkhe [50, 1921], Jentzch [20, 1924], Tause and Schulte [39, 1924], Moore [27, 1917], and Schaefer [37, 1931]. A review of the work of these experimenters has recently been given by Challoner [4, 1932]. The method has also been used widely for petrol and low boiling-point fuels, chiefly by Weerman [51, 1927], Egerton and Gates [13, 14, 1926], Thompson [40, 1928], Masson and Hamilton [25, 1927–9], and recently by Wiezovich, Whiteley, and Turner [49, 1935]. The possible variations in working, e.g. drop size, nature of surface, velocity of supporting atmosphere, &c., and the unknown factors corresponding with lag periods, have given rise to much discrepancy in published results; moreover, the method is complicated by the fact that prior to ignition the latent heat of evaporation of the droplet has to be acquired from the system. A further disadvantage is that it is not possible to define the precise mixture of combustible and air/oxygen to which the ignition relates. There has also been frequent discussion as to whether the molecules of a fuel when rapidly vaporized are in the same energized state as those of the stable vapour; in this connexion Egerton and Gates, who studied many of the factors influencing the ignition temperatures determined by the oil-drop method [14, 1927], have given the following figures:

Ignition temperatures

		I	II
Pentane admitted as	liquid drop	515	520
	vapour	655–90	685

The nature of the surface of the cup also appears to have a greater influence in this method than in others. Egerton and Gates gave the following figures showing the difference in behaviour of iron and silica:

	Iron	*Silica*
Petrol	450	470
Pentane	515	505
Acetaldehyde	395	350

On the whole there is some general agreement among the various observers, as the following figures show:

Ignition Temperatures (°C.) by Oil-drop Method

	Holm [19]	*Moore* [27]	*Tause and Schulte* [39]	*Masson and Hamilton* [25]	*Thompson* [40]	*Egerton and Gates* [13,14]
n-Pentane. .	..	..	487	579	309	515 (540)
n-Hexane. .	..	..	..	520	248	..
n-Heptane .	..	..	..	..	..	430
Benzene . .	520	566	740	656	580	700
Toluene . .	..	516	810	633	553	780
Ethyl alcohol .	510	518	558	568	426	515
Ethyl ether .	400	347	343	487	193	440
Petrol . .	..	383	..	..	353	460
Aniline . .	..	770	770	..	..	750
Carbon disulphide . .	..	..	..	343	125	120

It will be observed that Thompson's results are frequently much lower than those of other investigators; the explanation of this will be made clear later.

Until recently little study had been made of the influence of varying time lags on ignition temperature obtained by the oil-drop method, although this is an all-important question from the point of view of Diesel engines. Reference may be made to two recent papers on the matter by F. A. Foord [18, 1932] and by L. J. Le Mesurier [23, 1932]. Fig. 2 (Foord) shows the relationship between ignition temperatures and lag for the following fuels: (1) gas oil, (2) kerosine, (3) Diesel fuel A, (4) Diesel fuel B, (5) creosote.

4. **Ignition by Adiabatic Compression.** In 1903 Nernst [28] proposed measuring ignition temperatures by compressing gaseous explosive mixtures adiabatically. From the adiabatic equation $PV^{\gamma} = \text{constant}$, if γ be known, the temperature at any stage of the compression could be readily calculated from the relation:

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{1-\frac{1}{\gamma}} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}.$$

An advantage of such a method is that the walls of the vessel are comparatively cold, so that it may be considered free from any 'catalytic' influence. Moreover, it provides the possibility of measuring with accuracy the ignition temperatures for very short lags and in this sense approaches more nearly to actual engine conditions than any other method. It suffers in that cooling losses are heavy, and on this account there remains some doubt as to the exact temperature attained; in addition there is a little difficulty in deciding the accurate value of γ, and finally it has to be remembered that the ignition temperatures pertain to the compression pressure as well as to the corresponding temperature.

Working in Nernst's laboratories, Falk [16] in 1906 used the method to determine ignition temperatures of various hydrogen-oxygen mixtures, assuming *inter alia* that the mixtures detonated instantly and that the downward movement of the piston was arrested at the moment of ignition.

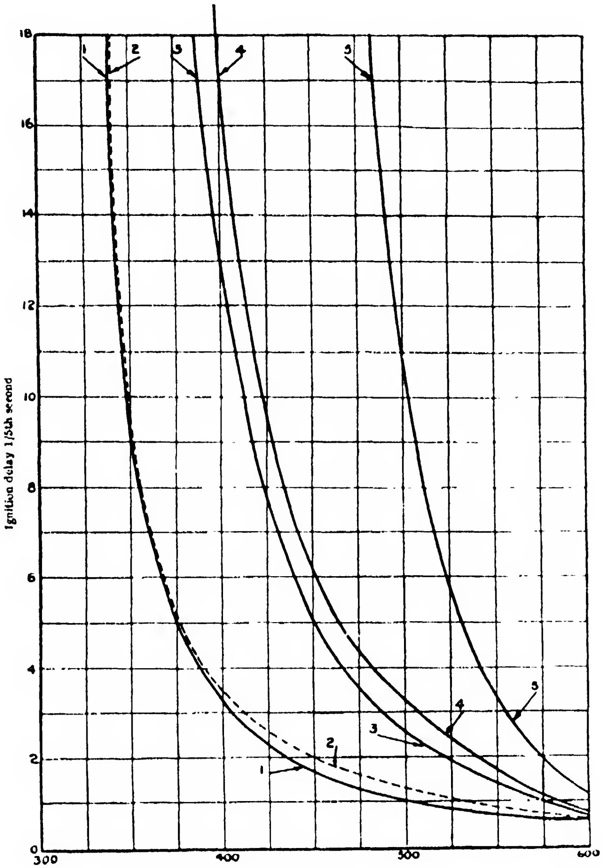


FIG. 2.

(*Reproduced by permission from* '*J. Inst. Petroleum Technologists*', **18** (1932).)

H. B. Dixon and J. M. Crofts [9, 1914] showed not only that few mixtures detonate in such circumstances but that the descent of the piston must be arrested at the moment the gases are brought to the true ignition point. During 1921–6 H. T. Tizard and D. R. Pye [42, 43] used a compression-ignition apparatus suited for experimenting with higher hydrocarbons under such conditions with a view to throwing some light on the knock problem. In their apparatus the compressing piston was not only arrested at the ignition point but firmly held so that no backward movement was possible during the delay period. Their more recent machine consisted of a cylinder (int. diam. = 3 in.), jacketed to maintain fixed initial temperatures up to 180° C., with a piston (stroke of 8 in.) whose motion was actuated by engagement with a heavy flywheel kept spinning by an electric motor at about 350 r.p.m. The apparatus was also provided with a pressure recorder so that pressure-time records were obtained during the compression-, delay-, and subsequent ignition and cooling-periods. It was thus possible to correlate the lags with the compression temperature, a matter with which we shall shortly deal.

The method has been used by other workers, notably Pignot [34, 1926–7] and Duchene [10, 1928], but experimental difficulties have retarded its more general application.

Spontaneous Ignition and Knock

Tizard and Pye's Experiments. In a paper on the causes of knocking in internal-combustion engines read before the North East Coast Institution of Engineers in May 1921 [41], Tizard described the compression and ignition machine designed and built by Ricardo and some preliminary results of ignition temperatures mainly for hydrogen-air mixtures. He pointed out that the values obtained by Dixon, which were calculated from the compression ratios with the ideal value of γ as if no loss of heat occurred, were too high and stressed the importance therefore of measuring the actual maximum pressures as well as the compression ratios. For hydrogen-air mixtures he gave the following minimum ignition temperatures:

Ratio Vol. hydrogen 4·76 vols. air	*Compression ratio, V_1/V_2*	*Pressure ratio, P_2/P_1*	*Ignition temperatures*		
			Initial temp., °C.	*Mean from PV, °C.*	*Calculated (Dixon) from V_1/V_2, °C.*
1·9	10·0	20·9	61	425	565
2·1	9·5	19·5	61	413	547
0·6	9·0	18·7	61·5	422	530
5·3	14·0	30·8	60	460	683
5·8	13·5	29·5	59·5	453	667

As regards hydrocarbon-air media, where the lags were much longer than with hydrogen-air mixtures, in the absence of any knowledge of the temperature gradients in the compressed gas Tizard accepted as best the value calculated from the recorded pressure, at the same time recognizing that some small portion of the gas in an unchilled zone might have a temperature corresponding with that calculated from the volume ratios. In determining the latter the ideal values of γ were calculated from the best-known specific heat data for the medium employed. The following were the so-calculated minimum ignition temperatures:

Hydrocarbon	*Parts by weight of fuel to 15 of air*	$\frac{V_1}{V_2}$	$\frac{P_2}{P_1}$	*Ideal γ*	*Initial temp., °C.*	*Ignition temp.*	
						Mean, °C.	*Max., °C.*
n-Pentane .	1·0	7·0	12·8	1·381	60	336	399
n-Hexane .	1·0	6·0	10·4	1·380	60	306	362
Cyclohexane	1·0	6·6	11·8	1·380	60	324	384
n-Heptane	0·8	5·5	9·34	1·383	59	291	325
	1·6	6·7	11·4	1·368	59	292	364
	0·4	8·0	15·8	1·391	13	292	348
	1·0	6·3	11·2	1·379	40	284	335
n-Octane .	1·0	5·0	8·2	1·379	60	275	321
Benzene	1·0	8·0	15·7	1·382	59	380	437
	1·0	9·1	18·7	1·382	40	373	430
	1·0	9·4	19·4	1·382	30	373	433

Tizard emphasized that the ignition lag decreases materially as the temperature attained on compression is raised; and as regards knock, in the discussion which followed his paper he stated his view as to the relation between the ignition temperature of a fuel and its behaviour in an engine as follows: '. . . Compression brings the charge to a temperature not very far short of its ignition temperature; the spark then passes, and owing to its higher temperature brings a portion of the gas . . . almost instantaneously to its maximum temperature. This will cause a still more violent turbulence; the hot portion will mix with the cooler portion with a high velocity *and brings the average temperature of the latter well above its ignition temperature. The rate of rise of pressure will then be very rapid.*'

In a second paper Tizard and Pye [43, 1922], on the assumption that an ignition temperature is that at which the heat production just exceeds the rate of loss to the surroundings, set out to determine from the observed lags prior to ignition the temperature coefficients of reaction velocity for various combustible media.

In the first place, from a study of the cooling curves for different gases compressed to corresponding temperatures they established that the rate of loss of heat was practically proportional to the difference between the average temperature of the gas and the temperature of the surroundings, i.e.

$$-\frac{d\theta}{dt} = \alpha(T-T_0).$$

On the assumption that the relation between reaction velocity and temperature obeys the Arrhenius equation $k = Ce^{-A/RT}$, equations were developed for the relation at different temperatures between the rates of cooling and the reaction velocity from which the time required for the reaction to reach completion from any initial temperature could be estimated. The times so calculated were in close agreement with the experimentally determined lags.

As a check on the method, in other experiments a fan was fitted to the explosion apparatus so that when running the cooling loss was increased; the results again agreed closely with experiment. The following are the calculated figures relating to heptane-air mixtures:

Heptane-Air Mixtures

Cooling factor $\begin{cases} \text{with fan} & \alpha = 1.42 \\ \text{without fan} & \alpha = 0.49 \end{cases}$

No fan		*Fan running*	
Ignition temp., °C.	*Delay (sec.)*	*Ignition temp., °C.*	*Delay (sec.)*
282	0·51	309	0·20
285	0·34	313	0·13
296·5	0·164	324	0·07
319	0·063	348	0·027
341	0·03	371	0·013
429	0·003	..	..

In the case of carbon disulphide-air mixtures the shortening of the delay periods with rise of temperature was much less marked or, in other words, the temperature coefficient was less.

Carbon Disulphide-Air Mixtures

No fan		*Fan running*	
Ignition temp., ° C.	*Delay (sec.)*	*Ignition temp., ° C.*	*Delay (sec.)*
255	0·98	298	0·34
258	0·70	301	0·25
269	0·38	312·5	0·13
290	0·19	335·5	0·07
311	0·105	358	0·04
395	0·021	..	..

The actual minimum ignition temperatures accepted by Tizard and Pye were those pertaining to the average temperature as deduced from the compression pressure, as follows:

	Heptane	*Ether*	*Carbon disulphide*
Average ignition temp.	280° C.	212° C.	253° C.

The values calculated from the volume ratios as if adiabatic conditions held would have been heptane 321° C., ether 243° C., and carbon disulphide 299° C. If it be more correct to assume that the portion of the gas responsible for ignition was at a temperature higher than the average temperature, then probably the true minimum ignition temperatures would proximate to a mean of the above figures as follows:

Heptane	*Ether*	*Carbon disulphide*
300° C.	227° C.	276° C.

Tizard and Pye incorporated some improvements in a more recent apparatus [43, 1926] as an outcome of experience previously gained; thus, in order to lessen the compression requisite for ignition, they employed, by suitably jacketing their machine, initial temperatures of 150–80° C. Also the indicator now employed was of the Collins type. It was concluded that ignition occurs very locally and no criterion of the temperature at this point can be inferred from the mean pressures as recorded by the indicator; for it was found that, in the majority of cases near the minimum ignition temperature, ignition might occur even though the mean compression temperature of the gas had fallen during the delay period. This is well illustrated by a close study of the pressure-time records illustrated in Fig. 3. This did not upset the conclusions drawn and the calculations previously made, however, for it may be concluded that the rate at which the nucleus of combustion is losing heat must bear some relation to the average rate for the whole gas.

Perhaps the most important aspect of Tizard and Pye's work is that it clearly shows that the conditions responsible for ignition when the lags are of the order of a fraction of a second are essentially thermal, or, in other words, a sufficiently high temperature alone is mainly responsible for the production of an adequate concentration of molecules sufficiently energized for reaction in accordance with the Arrhenius equation. And there does not appear in such circumstances to be the necessity for invoking branching chain mechanisms as being primarily responsible for ignition.

Generally speaking, the view put forward by Tizard and Pye as to the relationship between the knocking propensity of a fuel and its temperature coefficient of reaction when compressed above its ignition point has been accepted, though the violence associated with knock precludes the belief that it is merely a spontaneous ignition as ordinarily observed. The temperature coefficients of all paraffin hydrocarbons were found to be approximately the same, so that the compression-ignition temperatures should be a true measure of the tendency to knock. And just as the ignition temperatures of the paraffins were found to diminish as the series is ascended, so in practice the higher members give rise to knock more easily than do the lower ones. In fact the more rapid the rate of oxidation of the hydrocarbon the greater the tendency for it to knock.

Another interesting observation of Tizard and Pye is that whereas the minimum ignition temperature of carbon disulphide is lower than that of heptane the latter gives rise to knock more easily in an engine and, when corresponding mixtures are compressed adiabatically to temperatures *above* their respective ignition points, the development of pressure is far more rapid when heptane is used as the combustible.

Moreover, any factor which helps to reduce the temperature attained in the unburnt medium in an engine either locally or generally also reduces the tendency to knock. Thus increased turbulence or dilution with exhaust gas suppresses 'knock'. It is also more prevalent when heat conduction is poor, as when a cylinder is carbonized or when its proportions exceed a certain limit. The presence of constrictions or pockets where heat may accumulate has also to be avoided.

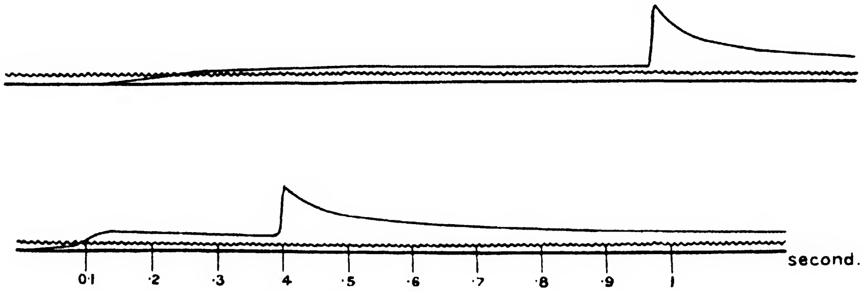


FIG. 3. Pressure-time records showing spontaneous ignition following adiabatic compression. (Tizard and Pye.)

Another interesting feature relates to the influence of the speed of running on the tendency to 'knock'. Thus 'knock' is more usually observed when an engine is labouring on hill-climbs; this has in some quarters been attributed to a better volumetric efficiency, but is mainly due to the increased available 'lag' period. The same explanation is probable in regard to observed variations in knock ratings with the speed of running of test engines (cf. R. O. King and H. Moss [21, 1931]).

A marked exception to the adequately high temperature explanation of knock has been the observation made from time to time in different laboratories that, on occasion, raising the working temperature may, in fact, suppress knock (cf. Fenning [17, 1925], Egerton and Gates [13, 1926], and Dumanois [11, 1933]). Actually it is now known that the higher paraffin hydrocarbons exhibit negative temperature coefficients over certain temperature ranges, so that the relationship between temperature coefficients and knock becomes if anything even more acceptable.

Until recently the most intriguing factor in knock had been the part played by pressure, for although it was early recognized that a limit was set to engine design by the limiting compression ratios (the Highest Useful Compression Ratios of Ricardo) beyond which it was impracticable to operate on account of the incidence of knock, no entirely satisfactory explanation of this had been forthcoming. From engine experiments it had been concluded that increase of pressure had a very marked effect, but it was difficult to distinguish between the two influences of pressure and temperature because increase of the one is always accompanied by increase in the other. Tizard and Pye were of the opinion that on the whole increase of pressure did lower ignition temperatures, though the effect was not marked. But they were also of the opinion that as their method only permitted pressure variation over a very limited range, it would be unwise to draw any conclusions from their own experiments without qualification; and it was stated (Tizard [43, 1926]): 'A question of considerable scientific interest is involved in the further exploration of the effect of pressure because it concerns the mechanism of the reaction between gases. But from a strictly practical point of view, if pressure has an effect as it seems to have, although to what extent is not known, it does not really matter whether its effect is caused by increasing the rate of reaction at low temperatures or by increasing the maximum temperature that is attained.'

It should here be mentioned that in 1926 H. L. Callendar and his collaborators [2] pointed out that vaporized hydrocarbons, and particularly those of high molecular weight, will tend to condense on compression and to form minute liquid drops ('nuclear drops'). Particularly would this be the case when the fuel is sucked in as a spray or when carbon particles are present, thus supplying nuclei which would initiate condensation. Moreover, the greater the compression ratio the greater would be the tendency of fuels to condense. In the case of a petrol such drops would consist of the heavier molecules having the lowest ignition temperatures; on absorbing oxygen they would become loci of chemical reaction and ultimately give rise to spontaneous ignition throughout the mass.

This view, which is admittedly in many ways attractive, threw open a new possible line of approach to the subject, but it was exposed to two serious criticisms pointed out by Tizard [43, 1926], namely, that (1) in an explosive mixture in an engine the hydrocarbon vapour is so far from being saturated that the possibility of liquid drops being formed is hardly admissible, and (2) in the majority of cases the compression temperature is higher than the critical temperatures of the hydrocarbons concerned. (See also Egerton and Gates [14, 1927]).

Townend's Experiments. The issue as to the relative influences of temperature and pressure remained indefinite for a number of years. In 1933, however, as part of an investigation into explosions of various hydrocarbon-air media at elevated temperatures and pressures, D. T. A. Townend and M. R. Mandlekar [44] commenced determinations of the influence of varying initial pressures up to 20 atm. on their reactivities during slow combustion up to their ultimate ignition points, and it was soon discovered that the relationship between ignition temperatures and pressure is by no means simple.

Generally speaking, previous determinations at atmospheric pressure of the ignition temperatures of mixtures of the paraffin hydrocarbons with air, as, for example, those of Mason and Wheeler [26, 1924], had shown them to be at *c.* 500° C.; under higher pressures, as in the experiments of Tizard and Pye [41, 1921; 42, 1926] (say, 12 atm.), they were usually at *c.* 300° C. Hitherto it had seemed reasonable to suppose that the fall in ignition temperature would be progressive with gradual increase of pressure, but Townend and Mandlekar found this to be far from the case; indeed, most of it was found to occur when a definite critical pressure had been attained, the exact value of which varied with the hydrocarbon concerned and with the composition of its mixture with air.

The method employed was that originating with Mallard and Le Chatelier [24, 1880], namely, admitting rapidly an explosive mixture under investigation into an evacuated vessel, maintained at an accurately known temperature, the apparatus being adapted to meet the requirements of high pressures. The explosion vessel consisted of a Ni-steel bomb provided with a mild-steel liner 15 cm. long by 4 cm. diam., the capacity being 190 c.c.; the mild-steel liner being replaceable as desired by one of glass, silica, aluminium, &c.

In discussing the results it should be borne in mind that the ignition temperatures at any pressure, unless otherwise stated, are the 'minimum' ignition temperatures, or, in other words, the lowest temperature to which the vessel must be heated for ignition ultimately to occur. The lags are therefore variable, depending upon the working conditions of temperature, pressure, and surface, a matter which, as previously explained, must receive due consideration when making inferences as to their applicability to engine conditions. For the purpose of this article we propose to describe as typical of the behaviour of the higher paraffin hydrocarbons the results obtained for hexane-air mixtures (Townend, Cohen, and Mandlekar [45, 1934]).

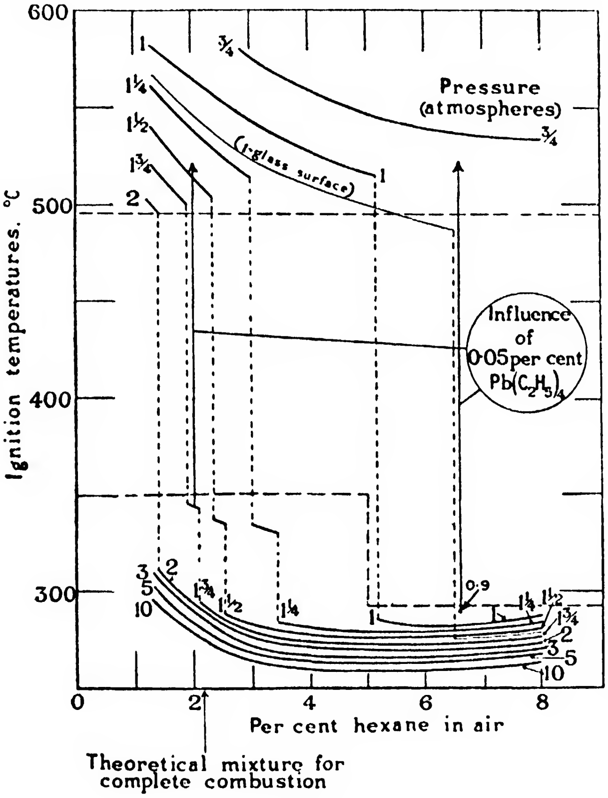


FIG. 4

(*Reproduced by permission from the 'Proceedings of the Royal Society'*, **146**, 115 (1934).)

In Fig. 4 a series of curves has been plotted showing the observed variation of ignition points with mixture composition for mixtures of hexane contents between 1 and 8% and at pressures of ¾, 1, 1¼, 1½, 1¾, 2, 3, 5, and 10 atm. It will be observed that the ignition temperatures lie in two well-defined groups, one above 495° C. and the other below (*a*) 350° C. for weak mixtures, (*b*) 290° C. for rich mixtures, as indicated by the horizontal dotted lines. Only at pressures below ¾ atm. did the ignition points for all hexane-air mixtures lie entirely in the upper group; thus increase of pressure to 1 atm. sufficed to lower to the lower group the ignition temperatures of all mixtures containing more than 5·2% of the combustible. This fact *inter alia* accounts for the conflicting and scanty data in the literature for ignition temperatures with this hydrocarbon. At pressures above 3 atm. the ignition temperatures for all mixtures are located in the lower group. It is thus clear that for any particular mixture there is a critical pressure at which the ignition temperature falls no less than about 200° C. from a higher system to a lower one, and it is to this critical pressure that the knocking propensity of a paraffin hydrocarbon is now seen to be related.

The influence of pressure on such ignition temperatures is perhaps best brought out by studying the detailed curves for individual mixtures. In Fig. 5, curves 1, 3, and 5 have been drawn showing the influence of progressive increments of initial pressure on the ignition points of mixtures having hexane contents 6·5, 2·7, and 1·8% respectively (theoretical mixture = 2·1%). To facilitate a proper understanding of the curves no. 5 may best be described.

It should be understood that ignition occurred at any temperature and pressure found in the area to the right of the curve (shaded side). At pressures up to 1·9 atm.—the critical transition pressure—the ignition points were located in the top range and fell progressively with increase of pressure to 502° C. At this pressure ignition also became possible at 345° C., but not at temperatures between 345° and 502° C. At 1·98 atm. ignition was possible at 298° C., between 340° and 352° C., and at all temperatures above 495° C. At about 2·4 atm. pressure the two lower ignition regions merged, so that ignition was possible at temperatures between 293° and 360° C. and above 470° C., but not between 360° and 470° C. At 4·6 atm. pressure ignition occurred at all temperatures above 280° C.

At pressures just exceeding the critical transition pressures ignition thus occurs at first only within limited temperature ranges which widen and ultimately merge with increasing pressure. This phenomenon has been found to be a general feature of the ignition of mixtures of the higher paraffins with air and becomes of increasing importance as the paraffins increase in complexity. Though quite unanticipated at the commencement of the investigation, this observation is in striking agreement with the work of Pease [32, 1929 and 1934] and Edgar [1, 1934; 35, 1929], and more recently of Neumann and Aivazov [29, 1935], who have all noted definite temperature ranges in which the temperature coefficients of reaction velocities of the oxidation of the higher paraffins are found to be negative (see article 'Combustion Phenomena of Hydrocarbons', p. 2860).

On comparing curve no. 5 with nos. 1 and 3 it will be observed that the regions in which the mixtures are non-ignitible are far more extensive for mixtures containing excess of air than for those containing excess of combustible; thus with the 6·5% mixture, curve 1, they lie merely between 0·85 and 1·29 atm. in contrast to the range 1·9 to 4·6 atm. for the 1·7% mixture, curve 5.

If oxygen be used as the supporter of combustion instead of air, curves of much the same type as those shown in Fig. 5 are obtained. The lower ignition regions, however, are now observed at much lower pressures than with air, so that at atmospheric pressure an ignition range is observed between *c.* 280 and 350° C. for mixtures of widely varying combustible/oxygen ratio; and above this range ignition is not possible until approximately 500° C. has been reached. This is in complete accord with the observations of Dykstra and Edgar [12, 1934] with hexane in oxygen at atmospheric pressure in a concentric tube apparatus.

The Influence of Anti-knocks. It is not within the purview of this article to deal with the possible mechanisms of anti-knocks, yet in so far as in practice addition of an anti-knock to a fuel enables its use at higher compression-ratios than would otherwise be possible, so if knock be related to temperature coefficients and ignition temperatures a corresponding inhibiting influence should be observable. Actually the matter has been studied by a number of investigators, and almost invariably the rate of oxidation of the hydrocarbon concerned has been found to be appreciably retarded by anti-knocks; as regards ignition temperatures, the following figures were determined by Egerton and Gates [13, 14, 1927] using the oil-drop method, who followed up the experiments of Weerman [51, 1927]:

Hydrocarbon	Ignition temperature ° C.	Rise in I.T. on addition of 0·025% by volume of $PbEt_4$ ° C.
Pentane . .	515	75
Iso-hexane .	525	46
Heptane . .	430	83
Benzene . .	(690)	18
Petrol (Shell) .	460	82

When it was discovered by Townend and Mandlekar that at a critical pressure the ignition temperature was lowered some 150–200° C. from a higher system to a lower one, it was at once appreciated that the presence of an anti-knock might tend to counteract the lowering effect; this assumption proved to be correct, as the following figures for a 2·4% pentane-air mixture show:

	Higher Range				*Lower Range*			
Initial pressure (atm.) .	1	1¼	1½	1¾	1¾	2	3	5
Normal ignition temperature	548	535	512	..	338	298	292	288
Ignition temperature on addition of 0·05% $PbEt_4$	574	553	538	509	..	343	298	293
Rise, ° C. . . .	26	18	26	171	..	45	6	5

The effect may perhaps be better understood by further reference to Fig. 5 in which curves 2, 4, and 6 relate to 6·5, 2·7, and 1·8% hexane-air mixtures to which 0·05% lead tetraethyl had been previously admixed. These curves do not maintain uniformly the precise contour of those of the undoped mixtures, but they reveal among themselves common features when compared with the latter, namely, (1) a general though not invariable increase in ignition temperature over the whole pressure range, and (2) *the necessity with the presence of lead tetraethyl for a higher pressure to effect ignition in the lower group.* This higher pressure has the effect of raising the ignition temperatures over a narrow pressure range (as shown by the vertical arrows) by about 175° C. for weak mixtures and about 230° C. for rich mixtures.

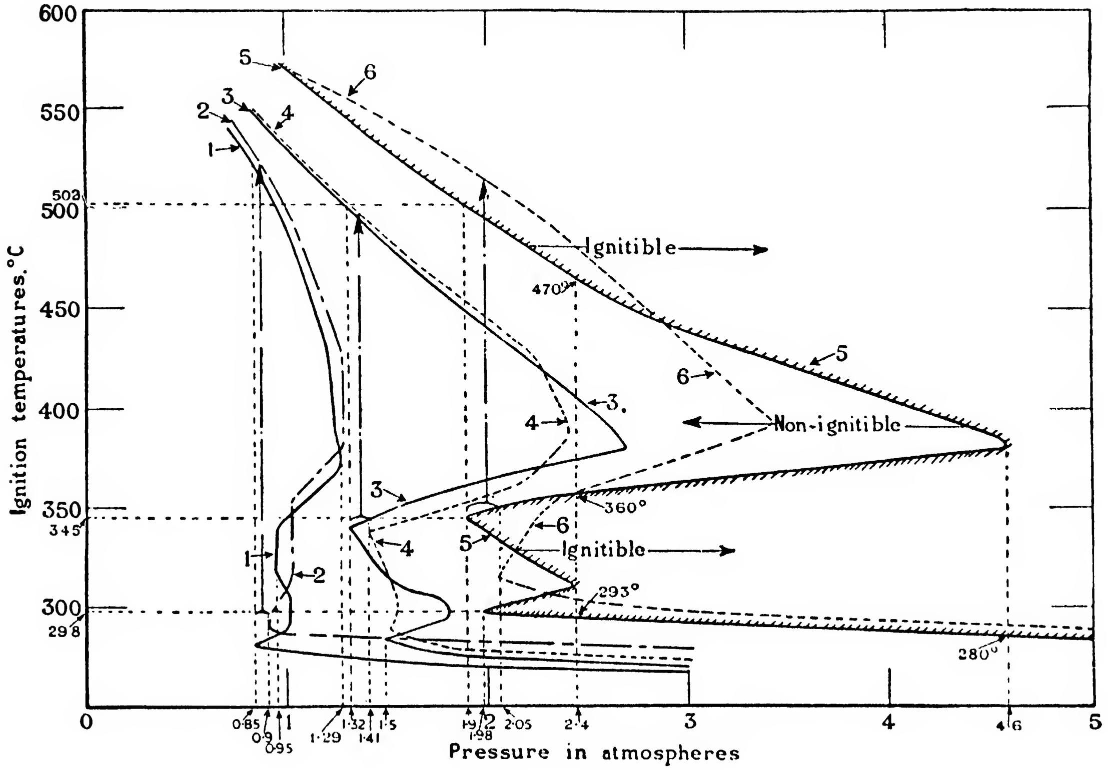


Fig. 5. Percentage mixtures for the curves: 1 = 6·5, 3 = 2·7, 5 = 1·8. The mixtures for curves 2, 4, and 6 were the same as those of 1, 3, 5, but with the addition of 0·05% *Pb* $(C_2H_5)_4$.

(*Reproduced by permission from the 'Proceedings of the Royal Society'*, **146,** 116 (1934).)

Cool Flames. An early observation in the investigation was that within certain limits of temperature and pressure a small pressure pulse was observable which was not comparable in intensity with the pressure developed on ignition. On fitting quartz windows to the apparatus the phenomenon was found to synchronize with the passage of a slow-moving bluish flame and the production of a considerable formation of intermediate products strongly aldehydic in character; it was quickly recognized as the so-called 'cool flame' first observed by W. H. Perkin, sen. [33, 1882] and studied during the last few years by a number of workers, notably H. J. Emeleus [15, 1926 and 1929], A. G. White [48, 1922], M. Prettre [36, 1932], and Beatty and Edgar [1, 1934; 35, 1929] (see also article 'Combustion Phenomena of Hydrocarbons', p. 2860).

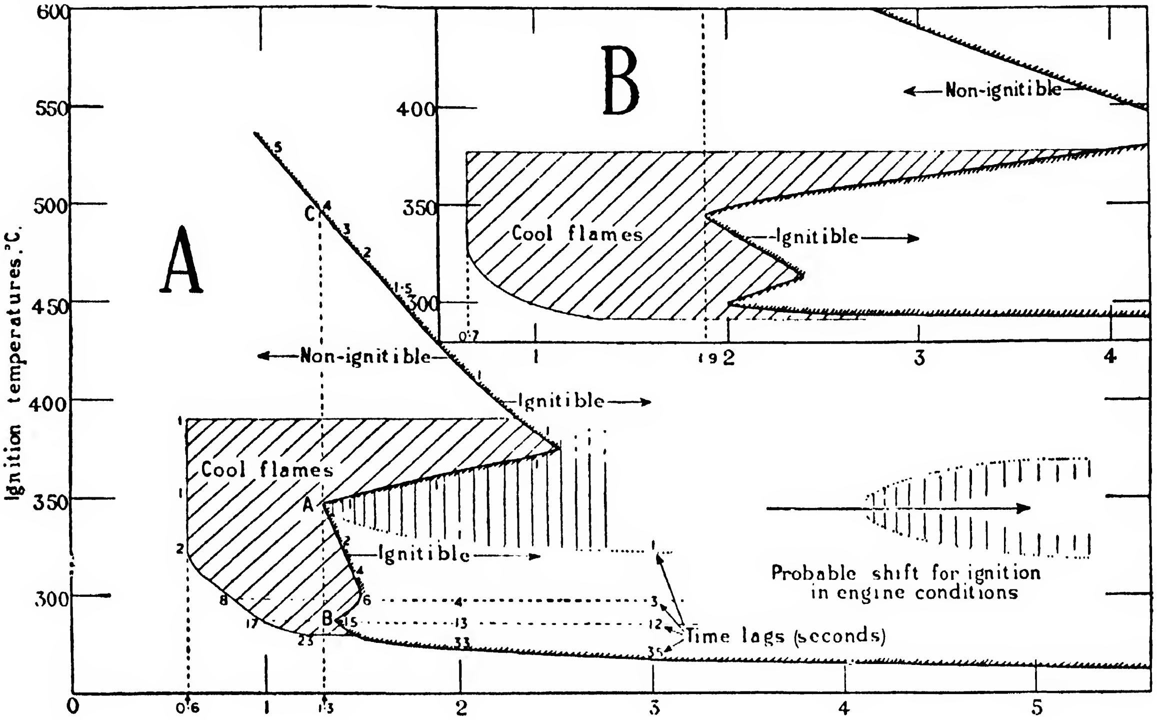


Fig. 6

(*Reproduced by permission from the 'Proceedings of the Royal Society'*, **146**, 118 (1934).)

The extent of the phenomenon in hexane-air mixtures may be illustrated by reference to Fig. 6, which relates to two mixtures, *A*, 3·1% mixture, and *B*, 1·8% mixture. The temperature and pressure limits within which it could be observed are illustrated by the diagonally shaded areas. Thus, with the 3·1% mixture, *A*, cool flames were first observed at 280° C. and at pressures between about 1·2 and 1·4 atm. Increase of pressure above 1·4 atm. resulted in true ignition as defined by the shaded boundary curve. Raising the initial temperature widened the lower pressure limit for cool flames to 0·6 atm. and progressively decreased the time lags until at 390° C. they became very short and the pressure pulses much less intense; at higher temperatures the phenomenon was no longer observable. With a 1·8% mixture, *B*, which contained an excess of air, the observations were much the same with the exception that cool flames did not occur at pressures below 0·7 atm., and the temperature range was now restricted to between about 290 and 380° C. Also, with the weaker mixture the cool flames were very much fainter and at the higher temperatures were detectable by the pressure pulse alone.

Fig. 6 also makes clear the relationship between the observations at atmospheric pressure of cool-flame temperature regions (usually 280–400° C.) and the true ignition temperatures (usually *c.* 500° C.). Thus Prettre [36, 1932], whose work covered many combustibles, employing a flow method at atmospheric pressure, showed that with the paraffin hydrocarbons 'première inflammations' were observable only within restricted temperature ranges in his experiments usually below 300° C., above which ignition was not possible until much higher temperatures had been reached. Similar observations have also been made by Coffey and Birchall [3, 1934], by Beatty and Edgar [1, 1934], and others. It is also important to note that apparent disagreement in the literature has sometimes arisen on account of a lack of discrimination among observers between true ignition and cool flames. As an example, Thompson's results [40, 1928] have to be considered in the light of his statement: 'The ignition temperatures were determined always by the appearance of flame, whether the combustion was of explosive violence or not. Sometimes the flame is barely visible; therefore, it proved advantageous to darken the room so that the flames could be better observed'; obviously, therefore, some of his ignition temperatures pertain to cool flames and not to true ignition.

Time Lags and Knock. As already mentioned, the ignition points determined in the pressure experiments are the lowest temperatures to which the vessel must be heated for ignition ultimately to occur, in which circumstances the lags may be not only appreciable but variable with experimental conditions. In Fig. 6 *A* the small figures along the ignition point and cool-flame curves relate to the observed time lags; these are seen to depend mainly on temperature. Thus as 2 atm. pressure, ignition point 274° C., the lag was 33 sec.; this decreased markedly as the temperature was raised, being 15 sec. at *B* (I.P. 285° C.) and approximately 1 sec. at *A* (I.P. 374° C.). This short lag remained constant until a temperature of approximately 420° C. had been reached; thereafter it increased progressively, being 4 sec. in the higher group at the critical transition pressure (*C*). These lags varied little with the mixture composition, tending generally to be shorter with mixtures containing an excess of air. There was a marked shortening of the lags, however, as the paraffin series was ascended, as the following figures for corresponding points (as in Fig. 6, *A*, *B*, *C*) on the curves show:

Hydrocarbon	*Time lags (sec.) at*		
	A	*B*	*C*
Butane . .	2	25	6 to 8
Pentane .	1·4	15	4 to 6
Hexane .	(approx.) 1	15	3 to 6
Octane . .	< 1	2	4 to 6

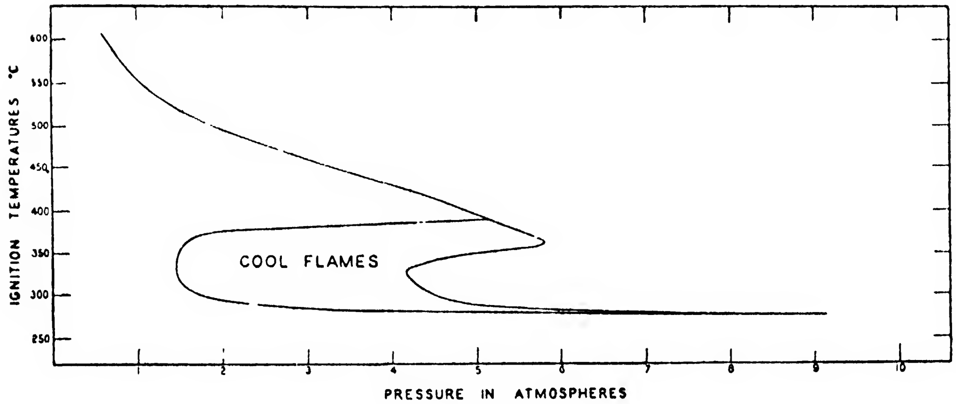


FIG. 7.

In considering the results in the light of their possible application to internal combustion engines where the time lag permissible would not exceed 0·005 sec. (say), the main interest attaches to (*a*) that portion of the curve exhibiting the shortest time lag and (*b*) the probable pressure conditions under which such short lags would be reduced to those corresponding with engine conditions. Actually, the portion of the curve (*A*, Fig. 6) having the shortest lag lies immediately above the point *A* (at about 350° C.). By increasing the pressure at temperatures below 350° C. ignition was found to occur with reduced time lag, and the boundary of the vertically shaded area is approximately the ignition-point curve for ignition with minimum lag. It seems probable that for ignition to occur within 0·005 sec. much higher pressures still would have to be employed, and a pressure shift somewhat as indicated by the horizontal arrow is visualized; these pressures would then approximate to the H.U.C.R.s observed in engine practice. Indeed, it may now be foreseen that much light will be thrown on many of the problems connected with both knock and also Diesel engines by the further exploration of the influence of progressive increase of pressure on lag periods prior to spontaneous ignition over wide temperature ranges, a programme of investigation which, when extremely short lags are considered, will call for the development of special technique.

As far as the work under review has proceeded, however, the critical transition pressures as determined in the manner described have exhibited an almost unfailing correspondence with knock ratings for like fuels, as found by engine tests. This correspondence may best be summarized as follows:

(1) The fall in ignition point at a critical transition pressure corresponds with the incidence of knock in an engine on the attainment of a definite compression ratio.

(2) Mixtures containing excess of combustible over wide ranges of composition are known to knock more easily than those with an excess of air; correspondingly much less pressure is necessary to transfer to the lower temperature system the ignition points of these mixtures than those of mixtures with an excess of air.

(3) The higher members of the paraffin hydrocarbons give rise to knock with less compression than do the lower ones. And the following are the critical transition pressures (atmospheres) for corresponding mixtures with air of the following hydrocarbons: ethane 14, propane 3 to 4, butane 1¾, pentane 1¼, hexane 1. Also, just as straight-chained paraffins are worse knocking fuels than the corresponding side-chain isomers, so the latter require higher critical transition pressures, for example, butane 1¾, *iso*-butane 3 to 4. In Fig. 7 the ignition point curve for a 4·7% *iso*-octane (2,2,4-trimethyl pentane) air mixture is shown, and may be compared with the curves for the hexane-air mixtures (Fig. 6, A and B).

The naphthenes which knock less readily than the paraffins bear the same relationship, for example, hexane 1, cyclohexane 1·5. And while the olefines do not exhibit the type of ignition-point curves characteristic of the paraffins (Figs. 5 and 6), increase of pressure causes a rapid fall in ignition temperature, so that if the pressure requisite for ignition at 350° C. (say) be employed as a criterion corresponding with the critical transition pressures observed with the paraffins, &c., the behaviour of olefines, naphthenes, and paraffins all fall into the same order as do their knock ratings. While the establishment of such a relationship between knock ratings and the corresponding critical ignition pressures needs no further elaboration, it remains to state that the ignition points of mixtures with air of non-knocking fuels such as benzene and methane have never been found to descend at all to the lower ignition system (i.e. below 400–450° C.) even at pressures up to 20–25 atm.

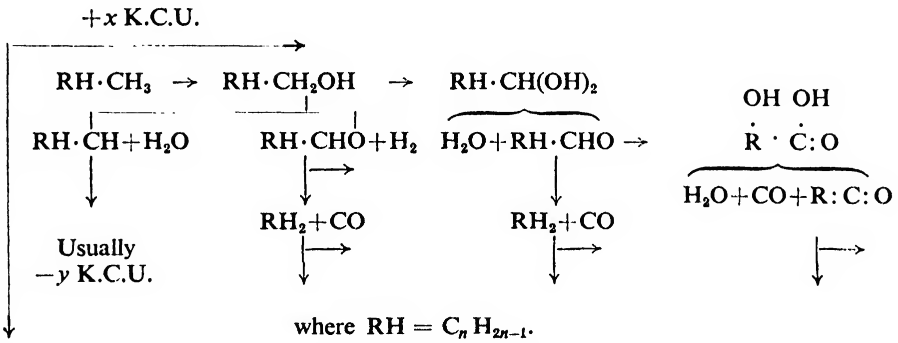
(4) The influence of an anti-knock in practice is to enable the compression to be raised before knock occurs; the increase in compression, however, is strictly limited. In the pressure experiments an anti-knock was found to raise the ignition point from the lower to the higher system only over a small pressure range; at higher pressures the ignition point remains in the lower system almost unaltered.

(5) In certain instances raising the working temperature has been found actually to suppress knock. Correspondingly, temperature ranges have been found in which ignition does not occur, although at lower temperatures it may do so.

The researches of Tizard and Pye [41, 1921–6] and of Townend and co-workers [44–6, 1934] may now be considered as complementary, for it is seen that the incidence of knock depends upon conditions both of adequate temperature and of adequate pressure. Thus, if circumstances allow of an adequate compression temperature, knock will be induced when an adequate compression ratio is employed; alternatively, if an engine be already operating with a sufficiently high compression ratio, knock will occur if a sufficiently high (but maybe not too high) temperature is reached. Finally, it is clear that knock depends upon conditions of adequate chemical reactivity in the unburnt explosive medium; but the precise mechanism of the phenomenon has yet to be established. There is little doubt, however, that compression waves play an equally important part (see article by R. P. Fraser on 'Flame Movement', &c., p. 2983), and it may be that knock can be regarded as a pseudo-detonation, less violent than true detonation (q.v.), in which an explosion wave may be propagated through a medium in an enhanced state of chemical reactivity and in which part of the chemical energy has already been expended.

The Mechanism of Ignition under Pressure. So far we have dealt with the nature of ignition phenomena under pressure of higher paraffin hydrocarbon, &c.—air media and their relationship with knock problems—without referring to the possible mechanisms of the chemical processes giving rise to them. And while we now propose briefly to give an outline of this aspect of the subject, it must be emphasized that much further investigation is needed before a full understanding of it can be reached; in particular, it is important to arrive at a true solution of the chemical mechanisms of (*a*) cool flames, and (*b*) the two distinct ignition systems, viz. that at high temperatures occurring at low pressures, and that in the cool flame temperature range with higher pressures.

According to Bone's hydroxylation view the oxidation of a complex paraffin hydrocarbon would be expected to proceed somewhat as follows (see also 'Combustion Phenomena of Hydrocarbons', p. 2860):



where RH = $C_n H_{2n-1}$.

The life of intermediate compounds so formed depends upon temperature, pressure, mixture composition, and catalytic influences, effects which by the work of Newitt and collaborators [30, 1932–3] on the pressure oxidation of methane, ethane, &c., have been demonstrated to be operative. And not until recentlv has it been appreciated that the velocity of combustion of a complex combustible cannot be considered independently of the behaviour under the experimental conditions of the products to which it gives rise.

A striking feature of recent work on the oxidation of the paraffins over wide temperature ranges (Edgar [1, 1934; 35, 1929]; Prettre [36, 1932]; Townend [45, 1933–4]) is that over the range *c.* 240–380° C., although at first aldehydes constitute the principal products and their rate of production increases with rise of temperature, a temperature of optimum concentration is found above which they become less prominent and ultimately are detected only in negligible quantities. Over the same temperature range, but not above it, cool flames are observed; at higher temperatures the oxidation first slows down and does not again become rapid until temperatures of about 450–500° C. have been reached.

The tentative view advanced by Townend and co-workers in regard to their pressure-ignition experiments is that the aldehydes produced during slow combustion are relatively unstable, there being a strong tendency to break down into carbon monoxide and the corresponding lower paraffins; and at initial temperatures above about 380° C. their existence (except perhaps with formaldehyde) is probably transient. The reaction velocity may be controlled therefore by the relative probabilities of (*a*) the further oxidation of aldehydes to acids, &c., and (*b*) the breakdown of aldehydes to carbon monoxide and corresponding paraffins, in which event the reaction would be arrested unless the temperature be adequate to permit the rapid oxidation of the breakdown products. This explanation accounts well for the two ignition-temperature systems; for the higher one probably pertains to the thermal decomponents of intermedially formed bodies known not to ignite below *c.* 500° C., and the lower ignition system would be established when pressure conditions allow of an adequate formation and survival of higher aldehydes. While such an explanation was based on a thermal interpretation of ignition, it is not inconsistent with the survival of (say) aldehydes giving rise to some chain mechanism as, for example, might result from the formation of per-acids during their secondary oxidations; all these aspects of the matter, however, need still further exploration and are considered in more detail elsewhere ('Combustion Phenomena of Hydrocarbons', p. 2860).

REFERENCES

1. Beatty, H. A., and Edgar, G. *J.A.C.S.* **56**, 103 (1934).
2. Callendar, H. L., and Collaborators. *Rep. and Mem. Aeronautical Research Committee*, 1062 (1926); *Engineering*, 147, 182, and 210 (1927).
3. Coffey, S., and Birchall, T. *J.S.C.I.* **53**, 267 (1934).
4. Challoner, J. L. *J.I.P.T.* **18**, 548 (1932).
5. Constam and Schlaepfer. *Z. der deut. Ing.* **57**, 39 (1914).
6. Coward, H. F. *J.C.S.* 1382 (1934).
7. Dixon, H. B., and Coward, H. F. *J.C.S.* **98**, 514 (1909).
8. Dixon, H. B., and Higgins. *Trans. Faraday Soc.* **22**, 267 (1926).
9. Dixon, H. B., and Crofts, J. M. *J.C.S.* **105**, 2036 (1914).
10. Duchene. *C.R. Acad. Paris.* **186**, 220 (1928); **192**, 1633 (1931); *J. usines gaz*, **55**, 524 (1931).
11. Dumanois, P. *C.R. Acad. Paris*, **197**, 393 (1933).
12. Dykstra, F. J., and Edgar, G. *Ind. Eng. Chem.* **26**, 509 (1934).
13. Egerton, A., and Gates, S. F. *Rep. and Mem. Aeronautical Res. Comm.* 1079 (1926).
14. —— —— *J.I.P.T.* **13**, 265 (1927).

15. Emeleus. *J.C.S.* 2948 (1926); 1733 (1929).
16. Falk, H. G. *J.A.C.S.* **28,** 1517 (1906); **29,** 1536 (1907).
17. Fenning, R. W. *Rep. and Mem. Aeronautical Res. Comm.* 979 (1925).
18. Foord, F. A. *J.I.P.T.* **18,** 533 (1932).
19. Holm. *Z. ang. Chem.* **26,** 273 (1913).
20. Jentzch. *Z. ver. deut. Ing.* **68,** 1150 (1924).
21. King, R. O., and Moss, H. *Engineering,* **132,** 177 (1931).
22. Laffitte, P., and Prettre, M. *C.R. Acad. Paris,* **187,** 763 (1918); **188,** 1403 (1929); **190,** 796 (1930); **189,** 177 (1929); **191,** 329, 414 (1930).
23. Le Mesurier, L. J. *J.I.P.T.* **18,** 562 (1932).
24. Mallard and Le Chatelier, H. *C.R. Acad. Paris,* **91,** 825 (1880); *Ann. Min.* **4,** 274 (1883).
25. Masson, H. J., and Hamilton, W. F. *Ind. Eng. Chem.* **19,** 1335 (1927); **20,** 813 (1928); **21,** 544 (1929).
26. Mason, W., and Wheeler, R. V. *J.C.S.* **125,** 1869 (1924); **121,** 2079 (1922).
27. Moore, H. *J.S.C.I.* **36,** 109 (1917); *J.I.P.T.* **6,** 186 (1920).
28. Nernst, W. *Theor. Chem.* Buch IV, Teil 4.
29. Neumann and Aivazov. *Nature* (1935).
30. Newitt, D. M., and Co-workers. *Proc. Roy. Soc., A,* **134,** 592 (1932); **140,** 426 (1933).
31. Norrish, R. G. W. *Proc. Roy. Soc., A,* **150,** 36 (1935).
32. Pease and Munro. *J.A.C.S.* **51,** 1839 (1929); **56,** 1034 (1934).
33. Perkin, W. H., Sen. *J.C.S.* **44,** 363 (1882).
34. Pignot, A. *C.R. Acad. Paris,* **182,** 376 (1926); **185,** 111 (1927). *J. usines gaz,* **56,** 594 (1932).
35. Pope, J. C., Dykstra, F. J., and Edgar, G. *J.A.C.S.* **51,** 1875, 2203 and 2213 (1929).
36. Prettre, M. *Bull. Soc. Chim.* **51,** 1132 (1932).
37. Schaefer. *Schiffbautechnische Gesellschaft.* Nov. 1931.
38. Taffanel and Le Floch. *C.R. Acad. Paris,* **156,** 1544 (1913); **157,** 469, 595, 714 (1913).
39. Tausz and Schulte. *Z. ver deut. Ing.* **68,** 574 (1924).
40. Thompson, N. J. *Ind. Eng. Chem.* **21,** 134 (1928).
41. Tizard, H. T. *Proc. N.E. Coast Eng.* **31,** 381 (1921).
42. Tizard, H. T., and Pye, D. R. *Phil. Mag.* **44,** 79 (1922); **1,** 1094 (1926).
43. Tizard, H. T. *Trans. Faraday Soc.* **22,** 360–2 (1926).
44. Townend, D. T. A., and Mandlekar, M. R. *Proc. Roy. Soc., A,* **141,** 484 (1933); *A,* **143,** 168 (1934).
45. Townend, D. T. A., Cohen, L. L., and Mandlekar, M. R. *Proc. Roy. Soc., A,* **143,** 168 (1934).
46. Townend, D. T. A., and Cohen, L. L. *J.S.C.I.* **53,** 267 (1934).
47. White, A. G., and Price, T. W. *J.C.S.* **115,** 1462 (1919).
48. White, A. G. *J.C.S.* **121,** 2561 (1922), &c.
49. Wiezovich, P. J., Whiteley, J. M., and Turner, L. B. *Ind. Eng. Chem.* **27,** 152 (1935).
50. Wollers and Emkhe. *Krupp's Monatsheft.* 1921.
51. Weerman. *J.I.P.T.* **13,** 300 (1927).

6. SPONTANEOUS IGNITION TEMPERATURES: DETERMINATION AND SIGNIFICANCE

By Wing-Commander W. HELMORE, Ph.D., M.Sc., F.C.S., M.Inst.P.T., A.F.R.Ae.S.
Engineering Laboratory, Cambridge University, England

THE increasing use of liquid fuels for both internal and external combustion has directed attention to a more intimate study of their combustion as influenced by chemical and physical characteristics. Among the many investigations which have been made, those concerning the so-called Spontaneous Ignition Temperatures or Auto-ignition Temperatures seem to possess those essentials necessary to shed additional light upon the mechanism of combustion, the internal structure of fuels, and the effect of chemical structure upon combustion characteristics.

The spontaneous ignition temperature of a liquid fuel may be broadly defined as the lowest temperature at which the fuel will ignite after a certain delay without the application of any artificial means of ignition. Either air or oxygen may be used as the supporter of combustion. When any combustible mixture is heated, the rate of oxidation increases until a stage is reached when the rate of gain of heat of a volume element of the vapour—due to exothermic oxidation reactions—balances the rate of loss of heat due to radiation and conduction to the surroundings. The 'ignition-point' of that volume element of the mixture is the temperature at which a heat balance is reached. If the temperature is exceeded, the reaction rapidly accelerates until the products are raised to a temperature such that an appreciable amount of energy is emitted in the visible regions of the spectrum. The vapour then inflames.

It was recognized in 1907 that there is no relation between the flash-point or burning-point of a liquid fuel and its ability to ignite spontaneously inside an engine cylinder, a characteristic or property depending primarily on its chemical character.

The earliest available determinations of spontaneous ignition temperatures were made by Holm [8] in 1913. By allowing drops of liquids to fall upon a heated porcelain surface, the temperature of which was measured by a thermocouple, the ignition temperatures (in air at normal pressure) of a number of common liquid fuels were determined. Holm found, in general, that simplicity of molecular structure is associated with high ignition temperatures, and also that the spontaneous ignition temperature is dependent upon the heat of decomposition and activity of free valences at the moment of splitting apart or rearrangement. The value of such determinations as a means of testing fuels for their suitability in engines was pointed out by Constam and Schlaepfer [3, 1913], who allowed drops of liquid fuels to fall into a platinum crucible in a gas-heated sand-bath. Holm came to the conclusion that the spontaneous ignition temperature was a valuable addition to the knowledge of the suitability of fuel oils for Diesel engines, but Constam and Schlaepfer did not share this opinion. They merely considered the results as an indication that at atmospheric pressure and in an open dish one could observe differences which various grades of fuel oil would show as a result of their chemical character, and not necessarily when igniting in a Diesel engine operating at much higher pressures.

At a somewhat later date, H. Moore [12, 1917, 1920] developed a form of spontaneous ignition temperature apparatus while engaged in a study of Diesel fuels. The apparatus employed consisted of a platinum crucible embedded in a steel block heated by a gas burner. Dry preheated air or oxygen was delivered at a constant rate to the crucible, the preheating being accomplished by a small coil in the steel block, through which the air or oxygen passed. This type of apparatus has been used extensively by subsequent workers—although various modifications have been made. By means of this apparatus Moore determined the spontaneous ignition temperatures of a number of substances, and from these temperatures estimated their suitability for use in the Diesel engine. The work of Moore was the first positive attempt to correlate ignition temperatures and engine behaviour, and the following conclusions were arrived at:

(*a*) Simple molecules have higher spontaneous ignition temperatures than similar compounds containing more complex molecules.
(*b*) Aromatics have higher spontaneous ignition temperatures than aliphatic hydrocarbons.
(*c*) Unsaturateds have lower spontaneous ignition temperatures than the corresponding saturated hydrocarbons.
(*d*) Ignition temperatures in air are higher than those in oxygen.
(*e*) Fuels for use in spark-ignition engines should have ignition temperatures as high as possible, and fuels for compression-ignition (i.e. Diesel) engines should have low ignition temperatures.

Tausz and Schulte [18, 1924] used a modification of Moore's apparatus and obtained valuable data on many pure compounds and common fuels—both in air and in oxygen, at both normal and increased pressures. Increase in pressure was, in general, found to lower the spontaneous ignition temperature, an observation agreeing with theory, as at elevated pressures the frequency of collision of the various molecules concerned is increased.

Early in 1924 Ormandy and Craven [15] described the results of experiments with a Moore ignition meter which had for their object an inquiry into the effect of 'anti-detonating' compounds on the spontaneous ignition temperature of fuels. These investigators found that such substances had little effect on the S.I.T. of pure *n*-heptane in oxygen. Two years later they determined the S.I.T.s of a number of pure compounds in oxygen in the same apparatus [16, 1926]. After the discovery of the valuable anti-knock properties of tetraethyl lead, a series of investigations on the theory of anti-detonants was published in which the significance of spontaneous ignition temperatures was thoroughly examined. The Moore S.I.T. apparatus has remained in vogue until the present day and is widely used.

Apparatus employed for the Determination of Spontaneous Ignition Temperatures and Effect of Operating Variables

The most important methods which have been employed for the determination of ignition temperatures are as follows:

1. Crucible methods—static and dynamic.
2. Dynamic tube methods.
3. Bomb methods.
4. Methods of adiabatic compression.

Of these the crucible methods are by far the most popular.

Crucible Methods.

As already mentioned, the Moore type of crucible is almost universally employed, a diagram of which, in a slightly modified form, is shown in Fig. 1.

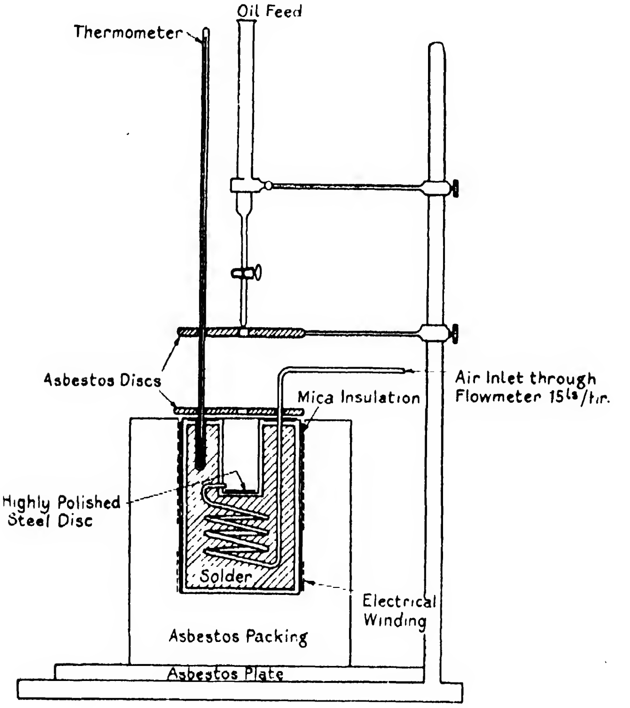


FIG. 1. Moore type spontaneous ignition temperature apparatus.

Moore originally employed a block of steel or cast iron, 100 mm. diameter and 75 mm. deep, the base of which was cut into deep grooves in order to present greater heating surface to a gas-burner flame by which it was heated. The top of the block contained a recess machined to accommodate a crucible 26 mm. diameter and 22 mm. deep, covered by a steel plate provided with two holes, one for the oxygen or air inlet and the other for the admission of the substance to be tested. The oxygen or air was passed from a container through holes drilled in the casting before entering the crucible and was thereby preheated to the temperature of the block. Temperature measurements were made by thermocouple. The procedure adopted in the determination of spontaneous ignition temperatures was as follows: When the temperature of the steel block became constant, one drop of the liquid substance under examination was allowed to fall on the bottom of the crucible by passing through a hole in the centre of the cover. The occurrence of an explosion or flame indicated that the temperature of the apparatus was above the S.I.T. of the substance tested and tests at lower temperatures were made. The S.I.T. of the substance was taken as the lowest temperature at which the substance ignited after an indefinite 'delay'. Moore also showed that the delay between introduction of a liquid fuel into the crucible and its ignition varied according to the temperature-high temperatures giving short-delay periods and vice versa. No special apparatus was employed for the measurement of delay periods—a simple stopwatch being employed. Typical temperature-delay period curves for various Diesel fuels, determined in a Moore type apparatus, are shown in Fig. 2.

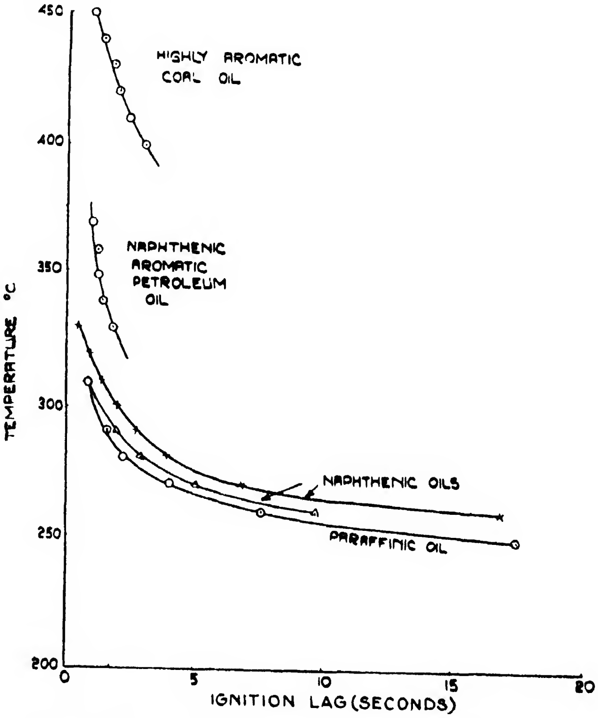


FIG. 2. Temperature-delay curves for various Diesel fuels.

Among the many users of the Moore apparatus the following have made slight modifications giving greater accuracy or ease of operation. Ormandy and Craven [15, 1924], Weerman [21, 1927], Masson and Hamilton [11, 1927], Wiezevich, Whiteley, and Turner [24, 1935], and Nash and Howes [13].

Krupp Ignition Meter.

The Krupp apparatus consists of an electrically heated crucible suitable for the determination of S.I.T.s up to 1,300° C. The ignition block is of Krupp's rustless steel provided with a conical-shaped cavity which eliminates lining materials, and the ignition space is uniformly heated. The oxygen or air supply is fed into the bottom of the ignition space.

Jentzsch Ignition Meter.

This apparatus is also of the crucible type, the crucible being of stainless steel situated in an electric furnace and divided into four symmetrically placed pockets of equal size. One of the chambers acts as a thermometer pocket, while the remaining three are used as ignition chambers, each being fed with oxygen from a central channel. In this apparatus the S.I.T. is taken as the lowest temperature at which self-ignition occurs in the presence of a rich oxygen stream, and means are provided for measuring the oxygen rate employed. A criterion of fuel quality, called the *Ignition Value*, is given by

$$Z = \frac{t}{b+1},$$

where Z = ignition value,
t = ignition temperature,
b = number of oxygen bubbles per minute.

Jentzsch ascertained that the tendency to ignite is greatly influenced by the oxygen flow rate employed.

American Society of Testing Materials Standard Test for the Determination of Spontaneous Ignition Temperatures

In 1930 a standard test was adopted for the measurement of ignition temperatures, A.S.T.M. Designation D. 286–30. This employs a glass conical flask (160-ml. capacity) heated in a solder bath over a gas flame. The quantity of liquid fuel added is variable, and the S.I.T. of the fuel is defined as the lowest temperature at which ignition occurs. Stagnant air is employed in the glass flask—no air stream being employed.

The Royal Aircraft Establishment (Farnborough) Spontaneous Ignition Temperature Apparatus

This apparatus, which may be described as belonging to the dynamic crucible type, was developed at the Royal Aircraft Establishment, Farnborough, and is generally known as the R.A.E. apparatus. It embodies many novel features and was specially developed for use in the testing of Diesel oils. It constitutes an attempt to simulate actual engine conditions in a simple apparatus operating at atmospheric pressure. Care has been taken to avoid contact between the fuel and metallic surfaces at a higher temperature than the air in the apparatus, because with regard to ease of starting in an engine, the walls of the combustion chamber are necessarily relatively cold in these circumstances and, unless a heated hot-spot is employed, ignition must take place in the air only. Under running conditions, of course, surface effect will be present in certain, if not most, engines, but any fuel which will ignite on emergence from the jet without ignition delay will ignite in air before it has time to travel across the combustion chamber to any heated surface.

The apparatus consists of (*a*) an electrically heated explosion vessel; (*b*) a fuel-injection system; (*c*) an injection-timing mechanism; (*d*) an explosion-timing mechanism; (*e*) and electrical recording mechanism for measuring the ignition delay; and (*f*) a thermocouple pocket for indicating the temperature of the air in the explosion vessel. The explosion vessel consists of a wrought-iron cylinder 6 in. diameter and 18 in. long, the sides of which are electrically heated by a resistance winding and suitably lagged and covered. The top end of the cylinder is formed of layers of steel and asbestos and carries the fuel-injection valve, thermocouple, a vent, and an air tube, and also a connexion for the explosion-time recorder. The fuel-injection valve (a standard Bosch Diesel engine unit) and explosion vessel are so arranged to give a spray having a cone angle less than the cone angle subtended by the perimeter of the bottom end of the vessel with the point of entry of the fuel into the vessel. This is necessary to ensure that the spray does not strike the heated sides of the vessel. The bottom end of the cylinder is of inverted conical shape, unlagged, and separated from the body part by a joint-ring of asbestos. This is necessary to ensure that any fuel from the jet which may impinge on the bottom does so on a relatively cool surface. The bottom end has a drain connexion to a vacuum pump or equivalent means for scavenging the vessel after each explosion. The air inlet is arranged tangentially to obtain a scavenging or circulating action and contact with the thermometric device.

The fuel-injection system consists of a standard Bosch nozzle testing apparatus, the pump being of the plunger type in which a small quantity of the fuel is trapped in the cylinder and forced past a spring-loaded non-return valve. The pump is operated by a falling weight and lever fulcrumed on the pump base, which ensures that the rate of injection of the charge is constant for each test.

Fig. 3 shows a photograph of the complete apparatus.

Method of Operation.

The temperature of the vessel having been raised to the highest temperature which it is desired to investigate, the current is cut off and sufficient time allowed for temperature conditions to become stable. A charge of cold air is then drawn into the vessel by means of a vacuum pump, the scavenging and circulation of the air being assisted by means of the tangentially offset induction port. Sufficient time is then allowed to elapse for the air temperature (indicated by the thermocouple) to reach a maximum and commence to fall off. The fuel is then injected by means of the retractable fuel injector nozzle, the time of injection and of the subsequent explosion being recorded electrically. The temperature and the time lag are thus measured, and tests are then carried out at lower temperatures. Between each test the products of combustion are drawn away and a fresh charge of air introduced. A series of readings are taken at 20–30° C. intervals until finally, at the lowest temperature, no explosion occurs after an indefinite delay.

This apparatus was used extensively by its originators in research on substances which reduce the ignition delay of Diesel fuels, and gave results which agreed to a reasonable extent with engine behaviour. However, it possesses the disadvantage, in common with all other types of spontaneous ignition meters, of not differentiating, to a sufficiently wide extent, between oils of closely similar values. A detailed description of the R.A.E. apparatus has been given by Foord [7, 1932].

Dynamic Tube Methods of Determining Spontaneous Ignition Temperatures

As the name implies, these methods consist of passing through heated tubes mixtures of air or oxygen with the substance being examined—the latter usually being in the gaseous phase—the temperature being raised until explosion occurs. Such methods permit of exact variation in the composition of the combustible mixture. Dixon [4, 1909] was among the first to use such a method, and Dykstra and Edgar [5, 1934] have recently examined the variables involved.

Bomb Methods for the Determination of Spontaneous Ignition Temperatures

Methods in which the ignition temperatures of fuels have been measured at elevated pressures in bombs have been used by Neumann [14, 1926], Tausz and Schulte [18, 1924], and Bridgeman and Marvin [1, 1928], but have not proved popular. The last-named investigators used a reaction vessel similar in shape and volume to a Liberty Aero engine

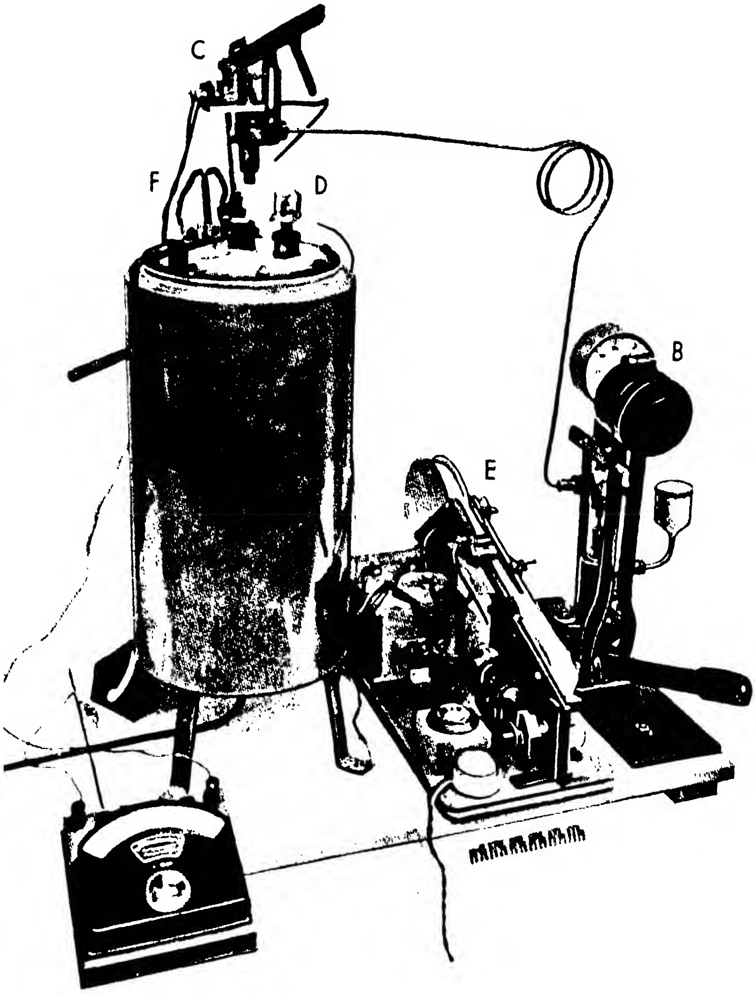


FIG. 3. The Royal Aircraft Establishment spontaneous ignition temperature apparatus

Reproduced from 'J. Inst. Petroleum Technologists', vol. 18, p. 543, 1932

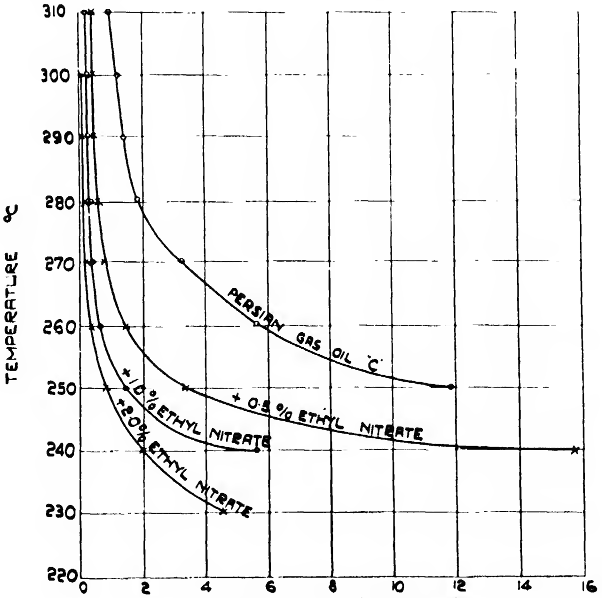


FIG. 4. Temperature-delay curves of blends of ethyl nitrate in a petroleum gas oil

increase in air-fuel ratio—generally causes a decrease in S.I.T. On the other hand, the above-mentioned work of Dykstra and Edgar [5, 1934] shows that in the lower ignition zone an increase in air-fuel ratio increases the ignition temperature.

Time Lag before Ignition.

This is one of the most important variables, since during this time interval thermal decomposition, synthesis of new compounds, and oxidation of the original fuel and the resultant products may occur. It is common practice to record as the spontaneous ignition temperature of a substance the lowest temperature at which ignition will occur—irrespective of time lag. This procedure is not recommended. In any S.I.T. determination the figures relating to ignition temperature and time lag should be recorded—in other words, the whole temperature-time lag curve should be given rather than the single temperature-point at indefinite delay time. It is not uncommon to find two substances of which *a* has a lower ignition temperature than *b* at one time lag, and a higher ignition temperature than *b* at another time lag.

Pressure.

Increasing pressure in general appears to lower the ignition temperature, but the effect of pressure on different fuels is so variable that no conclusions can be drawn as to the order of the ignition temperatures of a series of fuels under pressure from values at atmospheric pressure. It has been noted by several observers that the drop in ignition temperature with increasing pressure is not progressive, and that a sudden drop is obtained when some definite critical value of pressure is attained. In the case of butane-air mixtures there is, according to Newitt and Townend, a definite critical transition pressure at which the ignition-point is lowered suddenly by about 130° C. For all mixtures containing more than 3·5% butane (the theoretical mixture containing 3·1%) this occurs at 1·75 atm.; in all other cases a higher pressure is necessary, increasing as the butane content decreases.

The Spontaneous Ignition Temperatures of Pure Compounds and the Effect of Chemical Composition.

As already mentioned, there is little agreement shown in the literature for the spontaneous ignition temperatures of pure compounds, because of the wide variety of test methods employed and because far too little attention has been given to the effect of variables. On the other hand, the data available allow definite conclusions to be drawn regarding the effect of chemical composition upon ignition-points, and in particular has demonstrated that substances which are resistant to knocking in spark-ignition engines have high ignition temperatures, whereas those resistant to knocking in compression-ignition engines have low ignition temperatures.

The following conclusions may be arrived at:

1. The open-chain paraffin hydrocarbons have low ignition temperatures, the temperature decreasing with rise in molecular weight of the hydrocarbons.
2. The branched-chain paraffins—especially those of short open-chain length—have much higher ignition temperatures than the corresponding normal paraffins.
3. The olefines have variable ignition temperatures, but are often higher than those of the corresponding paraffins.
4. Naphthenes have, in general, higher ignition temperatures than those of *n*-paraffins and olefines containing the same number of carbon atoms.
5. The aromatic hydrocarbons have much higher ignition temperatures than other hydrocarbons, with the exception of branched-chain paraffin hydrocarbons such as 2,2,4-trimethyl pentane.
6. Alcohols possess higher ignition temperatures than the corresponding hydrocarbons—e.g. propylalcohol and propane, hexylalcohol and hexane, cyclohexanol and cyclohexane, phenol and benzene.
7. Aldehydes have much lower ignition temperatures than the corresponding hydrocarbons.
8. The introduction of bromine or chlorine atoms or nitro groups into the molecules of hydrocarbons leads, in general, to a reduction in ignition temperature; but, on the other hand, the introduction of amino groups causes a marked increase in ignition temperature.

These conclusions are in strict agreement with the results of tests in spark-ignition engines, in which open-chain paraffin hydrocarbons have considerable tendency to knock, whereas aromatics are resistant to knock. Moreover, amines are effective anti-knocks in such engines, whereas nitro compounds and aldehydes are knock inducers.

Typical values for the spontaneous ignition temperatures of various pure compounds are listed in the following table, in which all values relate to the simple Moore type apparatus, and are the lowest temperatures at which ignition occurred—irrespective of ignition delay.

Spontaneous Ignition Temperatures of Pure Compounds Moore Type Apparatus. (Typical values)

	In air, °C.	*In oxygen, °C.*
Hydrocarbons:		
n-Pentane	579	292
n-Hexane	520	286
n-Heptane	451	284
n-Octane	458	..
Iso-octane	561	..
Iso-dodecane . . .	564	..
Benzene	656	639
Toluene	633	582
Cyclohexane . . .	..	296
Naphthalene . . .	..	602
Alcohols:		
Methanol	574	488
Ethyl alcohol . . .	557	329
Iso-butyl alcohol . . .	542	326
Cyclohexanol . . .	..	322
Aldehydes:		
Acetaldehyde . . .	395	191
Miscellaneous:		
Diethylether	487	..
Aniline	620	..
Nitrobenzene . . .	556	..
o-Cresol	599	..
Chloroform	above 1,000	..
Ethyl bromide . . .	588	..
Bromobenzene . . .	688	..

The Effect of Knock Inducers and Knock Suppressors on Ignition Temperatures.

Ever since the discovery of the remarkable efficacy of tetraethyl lead as an anti-knock dope for spark-ignition engine fuels (i.e. gasolines) numerous attempts have been made to determine the precise mode of action of this and similar materials. Among such attempts, determinations of spontaneous ignition temperatures have been prominent.

Ormandy and Craven [15, 1924] were among the early workers in this field, and these investigators reported that in oxygen 'the addition of anti-detonating agents does not affect the ignition temperature to anything like the extent of their effect in an engine'. Some of their results were as follows:

Moore Apparatus—in Oxygen

n-Heptane (pure) . .	S.I.T. =	245° C.	Difference
+1% Xylidine . .	„	261° C.	Rise 16° C.
+1% *p*-Toluidine . .	„	259° C.	„ 14° C.
+1% Methylaniline .	„	251° C.	„ 6° C.
+0·25% Tetraethyl lead .	„	231° C.	Drop 14° C.
+0·25% Tetramethyl lead	„	236° C.	„ 9° C.

—the very contrary of what was to be expected.

Weerman found, however, in the same type of apparatus, using air instead of oxygen, that the addition of tetra-ethyl lead and similar anti-knock compounds to gasolines increased their spontaneous ignition temperatures to a considerable extent, as shown in the following typical figures:

Gasoline alone . .	S.I.T. =	335° C.	Difference
+0·5% Tetraethyl lead .	„	440° C.	Rise 105° C.
+1·0% „ „ .	„	465° C.	„ 130° C.
+2·9% Iron carbonyl .	„	505° C.	„ 170° C.
+1·0% Selenium diethyl .	„	475° C.	„ 140° C.

Results obtained by Egerton and Gates and subsequent workers confirm those of Weerman.

With regard to dopes for Diesel oils—i.e. substances which reduce the delay period between the moment of injection into the engine cylinder and the moment of ignition—the valuable properties of the alkyl nitrates and nitrites were first discovered at the Royal Aircraft Establishment, Farnborough, by ignition temperature determinations, and subsequent engine tests confirmed their efficacy. Fig. 4 shows the effect of small additions of ethyl nitrate to a petroleum gas oil upon the ignition temperatures and delay periods determined in a Moore type apparatus.

REFERENCES

1. Bridgeman, O. C., and Marvin, C. F. *Ind. Eng. Chem.* **20**, 1219 (1928).
2. Coffey, S., and Birchall, T. *J.S.C.I.* **53**, 245 (1934).
3. Constam and Schlaepfer. *Z. Ver. deut. Ing.* **57**, 1489, 1715 (1913).
4. Dixon, H. B. *J.C.S.* **95**, 514 (1909).
5. Dykstra, F. J., and Edgar, G. *Ind. Eng. Chem.* **26**, 509 (1934).
6. Egerton, A. C. G., and Gates, S. F. *J.I.P.T.* **13**, 273 (1927).
7. Foord, F. A. *J.I.P.T.* **18**, 533 (1932).
8. Holm, H. *Z. Angew. Chem.* **26**, 273 (1913).
9. Jentzsch, H. *Z. Ver. deut. Ing.* **68**, 1150 (1924).
10. Mason, T. N., and Wheeler, R. V. *J.C.S.* **125**, 1869 (1924).
11. Masson, H. J., and Hamilton, W. F. *Ind. Eng. Chem.* **19**, 1335 (1927).
12. Moore, H. *J.S.C.I.* **36**, 110 (1917); *J.I.P.T.* **6**, 186 (1920).
13. Nash, A. W., and Howes, D. A. *Principles of Motor Fuel Preparation and Application*, **2**, 459 (Chapman & Hall, Ltd.).
14. Neumann. *Z. Ver. deut. Ing.* **70**, 1071 (1926); N.A.C.A. Tech. Memo. 391 (Dec. 1926).
15. Ormandy, W. A., and Craven, E. C. *J.I.P.T.* **10**, 335 (1924).
16. ——— *J.I.P.T.* **12**, 650 (1926).
17. Report of A.S.T.M. Committee, D. 2, Sub-Committee xxviii (Chicago, 1927).
18. Tausz, J., and Schulte, F. *Mitt. chem. techn. Inst. techn. Hochschule Karlsruhe*, no. 2 (1924); *Z. Ver. deut. Ing.* **68**, 574 (1924).
19. Tizard, H. T., and Pye, D. R. *Phil. Mag.* (vi), **44**, 79 (1922).
20. Townend, D. T. A., and Cohen, L. L. *J.S.C.I.* **53**, 267 (1934).
21. Weerman, R. A. *J.I.P.T.* **13**, 300 (1927).
22. White, A. G., and Price, T. W. *J.C.S.* **115**, 1462 (1919).
23. ——— *J.C.S.* **115**, 1248 (1919).
24. Wiezevich, P. J., Whiteley, J. M., and Turner, L. B. *Ind. Eng. Chem.* **27**, 152 (1935).

7. IGNITION AND FLAME MOVEMENT

By **G. B. MAXWELL, M.C., B.Sc., Ph.D.**, *Anglo-Iranian Oil Company, Ltd.*, and **R. V. WHEELER, D.Sc.**, *Professor of Fuel Technology, University of Sheffield.*

PART I. IGNITION

THE oxidation of inflammable substances by air or oxygen often proceeds at comparatively low temperatures, but, owing to the dissipation to the surroundings of any heat generated, the rate of reaction does not materially increase as the oxidation continues. If, however, the heat evolved is not dissipated sufficiently rapidly, or if a sufficiently intense external source of heat be supplied, the temperature of the substance and of the air or oxygen will rise to a point at which flame appears.

The minimum value to which the temperature of a substance must be raised in order that inflammation may ultimately occur and be self-propagating is usually defined as the 'ignition-point' of the substance under the conditions of experiment. It is evident that the value of the ignition-point must be influenced considerably by the experimental conditions. Further, the value of the ignition-point as determined experimentally may be lower, often considerably lower, than the temperature at which inflammation finally occurs, the magnitude of the delay period before inflammation being determined by the manner in which the reaction velocity accelerates.

In the petroleum industry problems of ignition frequently arise. The most obvious problem is that of the ignition of the fuel in the internal combustion engine. This is by no means a simple problem, for there have to be considered not only the ignition by electric sparks of fairly homogeneous vapour-air mixtures in the petrol engine, but spark ignition of fuel sprays in the Hesselman engine, the ignition partly by compression and partly by contact with uncooled surfaces in the hot-bulb semi-Diesel engine, and ignition mainly by the heat of compression in the Diesel engine.

The ignition of inflammable dusts is a problem of safety with which such industries as coal-mining and flour-milling are concerned. Although the internal combustion engines were originally designed to run on coal dust, the practical difficulties proved too great and there does not seem to be any immediate likelihood of their being overcome. It is therefore not proposed to deal with the ignition of dusts in this article. Safety problems, however, are of paramount interest to the petroleum industry. The ignition of vapour-air mixtures in tanks during welding, or by frictional sparks or static electric discharges, has led to disastrous fires in the past, and a better understanding of the factors controlling such ignition is desirable.

Ignition problems can thus be studied from a number of different angles, whilst the results of experiments are likely to vary widely according to the viewpoint of the investigator and the nature of the apparatus and technique he employs. It is impossible, therefore, in a discussion of this nature, to give more than a qualitative description of the way in which various factors influence the ignition of gases and vapours. At the end of the article is given a short list of references.

Ignition of Homogeneous Gaseous Mixtures with Air and Oxygen

The ease of ignition and the ignition temperature of a gas-air mixture are determined by the following factors:

(i) The position, intensity, and nature of the source of ignition.
(ii) The chemical nature of the inflammable constituents and their amount relative to the concentration of oxygen available.
(iii) The nature and amount of any inert diluent gases present.
(iv) The presence or absence of substances which can catalyse the oxidation process.
(v) The initial temperature and pressure of the mixture and its state of motion (i.e. turbulent or stagnant).

The Source of Ignition. The ignition of a gas-air mixture can be effected in a variety of ways. An external source of heat such as a flame, hot wire, or heated surface may be brought in contact with the mixture; the inflammable constituents and the oxygen or air may be heated separately and then brought into contact; the mixture may be compressed rapidly and ignited by the heat of compression; frictional sparks may be produced or an electric discharge or arc may be passed in the mixture.

The position of the igniting source may influence ignition in two ways. The principal effect is on the limits of inflammability of the mixture, for with the source of ignition near the bottom of the vessel containing the mixture the limits are wider than when ignition is near the top. A secondary, indirect, effect arises from the possible damping action of any adjacent cold conducting surfaces. The intensity of the source of ignition is of moment particularly as regards electrical ignition, which will be discussed later.

The Nature of the Mixture and its Composition. Whatever the mode of ignition and the technique used to determine the ignition-points, provided comparisons are made under similar conditions, hydrocarbon gases and vapours tend to be rated in the following order of increasing difficulty to ignite: normal paraffins, naphthenes, olefines and branched chain paraffins, or aromatics.

In a given homologous series, ignition tends to become easier as the molecular weight increases, at all events when the normal representatives of each group of given molecular weight are compared. The branched chain compounds tend to have high ignition-points, the most symmetrical arrangement usually having the highest.

Whilst the ignition-point falls as molecular weight rises, it should be noted that the limits of inflammability usually narrow, this being in accordance with the general observation that the simpler the molecule of a combustible gas the wider are its limits of inflammability.

The effect of the composition of a mixture on its ease of ignition is complicated, for it varies with the character and even the position of the source of ignition.

When a transient igniting source, such as an electric spark, is considered, there are well-defined limits of composition of mixture for each inflammable gas, outside of which no inflammation can occur. A very intense transient source of ignition, such as a powerful condenser discharge across a spark-gap, may cause a local ignition in mixtures outside the normal range of inflammability, but the flame so generated will not travel far from the region of the spark-gap. When, however, the heat supplied as the igniting source is sustained, as when ignition is by a heated surface or by rapid compression, the more prolonged heating of the mixture before inflammation occurs may lead to thermal decomposition, giving rise to simpler molecules. Such products of decomposition usually have a wider range of inflammability than had the original gas. For this reason, when safety measures are being discussed, it would be unwise to accept values for the limits of inflammability of a gas based on experiments carried out in a different manner and with a different mode of ignition from that which might arise in the circumstances under consideration.

Within the normal limits of inflammability there is a marked difference in igniting power between transient and sustained sources of ignition. With spark ignition, electric or frictional, the most easily ignited mixture is usually not far removed in composition from that containing the theoretical amount of oxygen for complete combustion of the fuel. When, however, the ignition is effected by a heated surface or by compression, the ease of ignition usually increases as the mixture strength is increased. Simple gases such as hydrogen, which cannot undergo thermal decomposition, form exceptions to this general rule.

The Effect of Inert Diluents. The effect of the admixture of inert diluents with a given inflammable gas-air mixture is to reduce the oxygen concentration and to alter the thermal capacity and conductivity of the mixture. A reduction in oxygen concentration narrows the limits of inflammability of the combustible gas, mainly by lowering the upper limit. The effect of a reduction in the oxygen content on the ignition-point will depend partly on the initial composition of the mixture and partly on the mode of ignition. In general, the 'damping' effect of a given diluent is a direct function of its thermal capacity and conductivity, since these affect the temperature attained for a given liberation of heat and the rate of dissipation of heat at a given temperature.

The Effect of Catalysts. The action of traces of such negative catalysts as phenols on the oxidation of organic substances led to the suggestion that the action of pro- and anti-knocks in the internal combustion engine was an allied phenomenon. A considerable amount of experimental work has therefore been carried out on the effect of antiknock compounds such as lead tetraethyl on the slow oxidation of fuels in a heated enclosure. The most reliable evidence indicates that such compounds decrease the temperature coefficient of the oxidation, so that their effect is most marked at the high temperatures in an engine cylinder, in which but a short time is available for the reaction to develop into 'knock'. It is probable that the effect is due to the suppression of one or more possible side-reactions, such as, for example, the formation of organic peroxides as intermediate products.

There is, also, evidence of the catalytic effect of solid surfaces in promoting the ignition of gaseous mixtures. For this reason, when the heated enclosure method (or modifications thereof) is used for the determination of ignition-points, the enclosure should be made of quartz, since quartz shows little or no catalytic effect as compared, for example, with certain metals.

The Effect of Temperature and Pressure. As would be expected, the effect of any increase in the initial temperature of a gaseous mixture is to widen the limits of inflammability when ignition is effected by a transient source. In addition, the lag period between the moment of contact with the igniting source and the moment of inflammation is necessarily decreased. Ease of ignition is therefore increased by a rise in the initial temperature of the mixture.

The effect of increased initial pressure varies with the nature of the mixture and with the mode of ignition. Thus, with spark ignition of mixtures of air with hydrocarbon gases or vapours the range of inflammable mixtures is slightly extended as the initial pressure is raised. In general it appears that, with spark ignition, provided the arrangements allow of a spark passing in the denser medium, the ease of ignition will tend to increase slightly as the initial pressure is increased. When, however, ignition by means of heated surfaces is considered, there is usually found to be an optimum initial pressure for each inflammable gas at which the lowest ignition-point is obtained.

An increase in the initial density of a gas-air mixture facilitates ignition by compression and reduces the critical compression ratio for ignition to occur. This effect is due to the enhanced reaction velocity antecedent to inflammation (i.e. to a shorter delay period), so that heat losses are reduced. For this reason the more turbulent the mixture (and therefore the greater the opportunity for loss of heat) the greater the effect of density changes is likely to be.

The effect of motion of the gas-air mixture usually is to make ignition more difficult, the turbulence tending to increase the rate of dissipation of heat. This is particularly noticeable with electric spark ignition, for which much more powerful sparks are required when the mixtures are turbulent. Once ignition is effected, however, the subsequent inflammation is more rapid. The limits of inflammability tend to be extended somewhat in turbulent mixtures. In ignition by compression, the critical compression ratio for ignition tends to be raised by turbulence, owing to the increased heat losses, but the reverse may hold when any heated surface is available from which the mixture can abstract heat.

Electrical Ignition

Electrical ignition displays certain peculiarities that warrant separate consideration, though no more than a brief outline of the subject is given here. There are three principal types of electrical ignition to consider: ignition by high-tension 'jump' sparks, by static discharges, and by low-tension transient arcs.

Ignition by High-tension 'Jump' Sparks. Ignition in the petrol engine fitted with coil or magneto is by a 'jump' spark. The actual mode of ignition by a jump spark is still not fully understood, evidence having been adduced both for a purely thermal effect of the spark and also for ionization due to electrical rather than to thermal effects. The jump spark can be resolved, by oscillographic means, for example, into two components, an initial 'capacity component', similar to a condenser discharge, followed by an 'inductance component', similar to a transient low-tension arc. Ignition is mainly determined by the capacity component. ([Cf. Bradford, Finch, and Prior, *J. Chem. Soc.*, 230, 1933] Ed.)

The 'incendivity' of a high-tension jump spark is mainly determined by the following factors:

(i) The capacity of the gap circuit, including that of the secondary winding. This can be varied by varying the arrangement of the apparatus, but is independent of the magnitude of the primary current.

(ii) The voltage at which the spark is generated. This depends on the shape and disposition of the sparking points, on the nature and condition of the gases between them, and on the rate of application of the voltage. This last factor is influenced by the current in the primary circuit, particularly when sharp-pointed electrodes are used to form the gap.

It is possible, therefore, particularly between pointed electrodes, to alter the incendivity of the spark from a given coil across a given gap by altering the primary current. In such circumstances it is found that, for each mixture under standard conditions, there is a minimum primary current for ignition to occur when the spark is passed. Similarly, there is a minimum width of spark-gap for ignition of a given mixture for each value of the primary current above its minimum value. It is thus possible to measure the relative ignitibilities of various mixtures either by determining the minimum primary current for ignition with a given gap or by determining the minimum width of gap with a given primary current. The observations made previously in this article on the effect of various factors on ignition by electric sparks have been based on experiments carried out in this manner.

Ignition by Static Discharges (Frictional Electricity). The information available as regards ignition due to static discharges developed by friction is very meagre, though there is evidence that explosions and fires may have been caused in this way. The frictional effects between liquid streams and solid surfaces are capable, in certain circumstances, of developing sufficient potential to cause a flash-over, and the incendivity of the discharge is then determined by the same factors as determine the incendivity of the 'jump' spark, the most important factor being the capacity of the system. When pumping a liquid fuel from a delivery truck, therefore, the truck should be earthed.

It is also possible to develop quite a high potential on the metal nozzle of a high-pressure gas-line when the line is of some insulating material. Sparks can then be drawn from the nozzle if an earthed conductor is approached to it, but the incendivity of the sparks is low unless an external capacity is coupled across the spark-gap. Attempts to ignite firedamp-air mixtures from compressed-air pipes in this manner failed under conditions resembling those of practice, except when much dust or drops of liquid accompanied the compressed air.

Ignition by Transient Low-tension Arcs. The total energy which must be dissipated to cause ignition of a given mixture by a transient low-tension arc is considerably higher than with a high-tension jump spark. This is in accord with the view that has been advanced that the initial 'capacity component' of a jump spark is mainly responsible for ignition, and can be explained by reason of differences in the rate of delivery of heat energy by the two types of sparks. It should be observed that the energy required in a transient arc to cause ignition is independent of the nature, direct or alternating, of the current in the circuit broken.

Ignition by Frictional Sparks

The ease of ignition by frictional sparks depends upon the nature and temperature of the solid particles forming the sparks, upon the space density of such particles, and upon their rate of travel through the inflammable mixture. The greater the heat capacity and temperature of each spark, and the greater their concentration within a given volume of the inflammable mixture, the greater is the chance of that volume of mixture being raised to the inflammation temperature. Since there is a delay period between the ignition-point and the inflammation-point, it is essential for inflammation that the time of contact of the sparks with a given volume of the mixture should be adequate. Ignition may not take place when a shower of brilliant sparks travels freely through an inflammable mixture, but some obstruction in the path of the shower may cause ignition by prolonging the time of contact.

Ignition of Fuel Sprays or Mists in Contact with Air

In the ignition of fuel sprays, it is necessary to consider ignition by the electric spark, as in the Hesselman engine and in certain types of small oil-fired domestic heaters for central-heating plants; ignition by a heated surface or by glow-plug; and ignition by compression. In many so-called compression-ignition engines a combination of the last two types of ignition occurs, whilst the hot-bulb semi-Diesel engine relies on the presence of uncooled surfaces for its running.

The Ignition of Fuel Sprays by Electric Sparks. The ignition of fuel sprays by electric sparks does not appear to have been studied experimentally, and only observations from general experience are possible. In oil-heaters used for domestic purposes the spray, mixed with a current of air, is blown across a spark-gap where a train of sparks from an induction coil operated by a trembler is used for ignition. Fairly fine 'atomization' of the fuel is necessary to avoid quenching the sparks, but, owing to their intensity and continuity, a zone of high temperature is maintained in the path of the spray.

In the ignition of a fuel spray by an electric spark in an engine there is considerable difficulty in raising a sufficient quantity of fuel and air to the requisite temperature. It is not practicable to use a prolonged train of sparks, because of the difficulty of timing, and the liability of a single spark to be quenched by the fuel spray is great. The necessity of a special type of sparking-plug in the Hesselman engine, and the sensitivity of this engine to rapid changes of load, illustrate this difficulty. There seems to be no necessity to postulate the vaporization of the fuel previous to ignition, either in this or in the compression-ignition engine. Provided that the spark is hot and 'fat' enough to heat up a sufficient amount of oxygen, reaction will proceed readily enough at the surfaces of the liquid droplets. There is considerable evidence, from measurements of ignition delay in compression-ignition engines, that the volatility of a fuel, over a wide range, has no appreciable influence on the ease of ignition (cf. Article 18).

Whereas for the ignition of homogeneous gas-air mixtures there are well-defined limits of inflammability outside of which ignition and flame propagation will not take place, with fuel sprays only the nature of the igniting source, the temperature and pressure of the air, the distribution of the spray, and the degree of atomization determine ignition and inflammation. Whatever the amount of fuel injected into the hot compressed-air charge, those particles that come into contact with oxygen under the correct conditions will ignite; whether or no the ignition will propagate and the combustion approach completion is then entirely a matter of the size of the fuel droplets and their distribution with respect to the available oxygen.

Ignition by Glow-plug or by Heated Surfaces. It is usually found necessary to fit electrically heated glow-plugs in the air-cell or precombustion-chamber type of a compression-ignition engine for starting from cold. This is to counter the chilling of the air charge which occurs partly in the throat or transfer passage and partly in the air cell during compression. The hot-bulb semi-Diesel engine is usually started by cartridge or by the heating of a starting-tube by a blow-lamp. The subsequent running of this type

FIG. 1

FIG. 2

FIG. 3

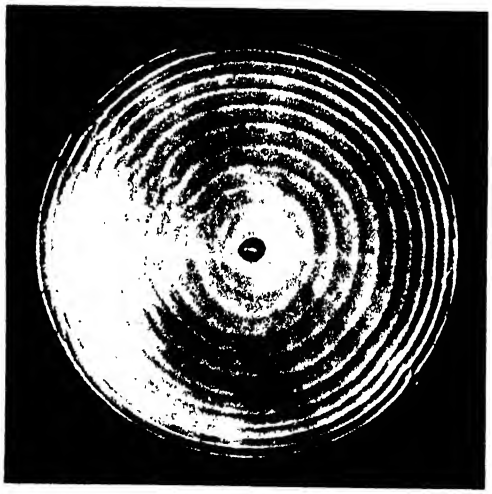


FIG. 4

FIG. 5

of engine is, as its name implies, by the contact of the charge with uncooled metal surfaces. These are usually at a dull red heat during full-load operation.

Experience with this type of engine indicates that the best operation, and the greatest freedom from coke formation and exhaust smoke, are obtained when the design is such that the air is heated by the surfaces and the fuel sprayed into the heated air, rather than when the fuel is sprayed directly on to the hot surface (cf. Article 18 in this section).

As in compression-ignition proper, the ignition-point and the delay on ignition between the injection of the fuel and the beginning of rapid combustion are both affected by the nature of the fuel, much as the nature of the fuel affects the ignition of homogeneous vapour-air mixtures. Thus, the aromatic fuels from asphaltic base crudes present greater difficulty of ignition and have longer ignition delays than are experienced with any other class of hydrocarbons.

For a given amount of fuel injected, the relative concentration of oxygen is proportional to the compression. Thus the compression has a marked effect on the ignition delay, and influences the starting of a compression-ignition engine to a more marked extent than does the compression in a spark-ignition engine.

Similarly, the effect of inert diluents is marked, owing to the reduction in oxygen concentration. In a two-stroke compression-ignition engine excessive exhaust back-pressure is a well-known cause of poor performance, owing to the increased amount of inert residual gases in the cylinders at the end of the exhaust.

The special features of ignition of fuel sprays or mists which have been examined experimentally with a view to determining their effect on ignition and combustion include the atomization of the spray, the volatility of the fuel, and the nature and degree of relative motion of the fuel and air charge. In closed-vessel experiments, carried out with no turbulence, or with very little as compared with engine conditions, there is evidence to show that the fineness of the spraying and the volatility of the fuel both directly affect the ease of ignition and the duration of the delay period. Under engine conditions of high turbulence and high fuel velocity, with the extremely small time periods available, the balance of the evidence seems to be against there being any appreciable effect on ease of ignition or ignition delay of either atomization or fuel volatility, or any direct effect of turbulence. Turbulence, by affecting the heat transfer between the air and the confining walls, has an indirect effect.

Though the air temperature does not affect the ignition-point of a given fuel, it naturally has a direct influence on the ignition delay. Thus, in a compression-ignition engine, since the smoothness of running is a direct function of ignition delay, every effort is made to raise the air-charge temperature to the highest value possible before fuel injection begins. The compression ratio must be as high as is consistent with the permissible weight and stiffness of the engine and, in such circumstances as obtain in the air-cell type of engine where the charge during compression is forced through a transfer passage, provision is usually made for some heat insulation of the walls of the passage; this tends to make the engine smoother in operation, particularly when running under varied loads such as in a vehicle.

Just as with spark-ignition of a homogeneous vapour-air mixture in a petrol engine there are substances such as lead tetraethyl or amyl nitrite which, in minute concentration, can considerably affect the running of the engine, so in the compression-ignition engine the same substances produce a marked difference in the smoothness of running. The concentrations of the substances required, however, are much higher, and their effects are exactly opposite to what they are in the spark-ignition engine. This reversal of the effect of 'catalysts' is in accordance with the well-known fact that aromatic fuels provide smooth running in a petrol engine, but very noisy running in a Diesel engine, particularly in small high-speed engines for which the permissible ignition-delay period is so short.

PART II. THE MOVEMENT OF FLAME

In general it is not sufficient to know the average rate of movement of the flame front to obtain a true picture of the nature of the inflammation of a combustible mixture. Only under rather special conditions is the speed of flame uniform, so that, unless the average rate over the whole path can be measured, measurements over a small section may be entirely misleading. This is particularly true when vibrations of the flame occur. Methods of measurement of flame speeds based on the registration of the arrival of the flame front at various points in its travel have therefore largely been superseded by photographic methods which enable records to be taken of the vagaries of the flame during its passage. Only in circumstances which preclude the direct observation of the flame are the older methods employed.

The revolving drum continuous photographic method, first used by Mallard and Le Chatelier and improved by H. B. Dixon, gives a clear picture of the movements of the flame front by focusing the image of the flame on a strip of sensitized paper wound on a revolving drum (see Fig. 1). This method has the disadvantage that subsequent events occurring in a region through which flame has already passed are difficult to interpret, and the records themselves may be unconvincing to those not familiar with the method. The 'snap-shot' method developed in the Safety in Mines Research Board's Laboratories (see Fig. 2), in essence a form of cinematography using a special type of extremely rapid camera shutter, overcomes these disadvantages, and it is surprising that it has not been more extensively employed in such work as the recording of the travel of flame in the cylinders of internal combustion engines.

The Inflammation of Homogeneous Gas-air Mixtures

The rate and nature of flame movement in a given gas-air mixture can vary widely with the conditions of experiment, and the factors determining them are complex. The subject has been simplified, however, by the conception of 'fundamental flame speed' which has recently been introduced.

This conception has arisen in the following way. When an inflammable gas-air mixture is ignited in a suitable manner at the open end of a tube which is closed at the far end, the flame usually travels for some distance at a sensibly uniform rate. Each succeeding layer of unburnt gas is raised to its inflammation point by conduction and radiation from the adjacent burning layer, and there is no appreciable movement of unburnt mixture, since the products of combustion are free to expand and escape from the open end of the tube. The rate of flame propagation during this 'uniform movement' would therefore be expected to be determined solely by the flame temperature, the thermal conductivity of the mixture, and the average rate of reaction in each layer of mixture during its heating-up period. In addition, however, it is found, on experiment, that very slight disturbances can have a disproportionately large effect on the rate of uniform movement, and that it is possible for a given mixture, under a given set of experimental conditions, to show two distinct rates of uniform movement in successive experiments.

The 'snap-shot' photographic method of studying flames has shown that the shape of the flame front and its area were affected by the slight disturbances that influenced the rate of uniform movement (see Fig. 3). From the photographs it was possible to measure the area of the flame and the rate of flame propagation, and thus to calculate the volume of mixture consumed in unit time. It was then found that, during the uniform movement of flame in a mixture initially at a given temperature and pressure, the volume of mixture consumed per unit area of flame was a constant whatever the speed of uniform movement in that mixture. Expressing this finding in a different manner, if each square centimetre of the area of the flame in a given mixture consumes x c.c. of mixture per second, the flame speed through the mixture, assumed at rest and at constant temperature and pressure ahead of the flame, will be x cm. per second. This value has been termed the 'fundamental speed' of flame in the given mixture under the given conditions of temperature and pressure.

From this treatment of the subject it is seen that any factor which influences the area of the flame will influence its speed in a proportionate degree. Further, any movement in the mixture ahead of the flame, due either to expansion of the burnt products or to some external agency, will add its effect to the fundamental flame speed. The area of the flame is determined by the shape and size of the combustion chamber and by the presence or absence of leaks or vents. In addition, both the area of the flame and the state of motion of the mixture are influenced by the freedom of expansion of the burnt products and by the effect of convection currents and of any forced turbulence due to external causes.

The speed of flame in any inflammable gas-air mixture will therefore be influenced by the following factors:

(1) The nature and concentration of the inflammable gas, since these determine the rate of reaction previous to inflammation. The rate of reaction is also affected by the rate of heat transference by conduction and radiation.

(2) The initial temperature of the mixture, since this influences the amount of heat required to reach inflammation point. The effect of an increase in the initial temperature from, say, 15° to 100° C. is, however, small.

(3) The initial pressure of the mixture. The effect is small because, though the rate of mass reaction increases proportionately with initial pressure, the density of the medium is also increased at the same rate. Thus the volume of mixture burnt per unit time, i.e. the rate of flame movement, is but little affected by density changes. When the flame reactions involve an increase in the number of molecules present, an increase in initial pressure tends to decrease the reaction velocity and thus the flame speed.

(4) The shape and size of the combustion chamber and the presence or absence of leaks or vents. If the products of combustion are unable to expand freely in the direction opposite to that of the movement of flame, the expansion causes a surge in the unburnt mixture. This surge accelerates the rate of flame propagation in an exponential manner until the free expansion is checked by the compressive influence of the walls of the combustion chamber. In the initial stages of travel of the flame, provided that no marked impetus in any particular direction is given by the igniting source, there is no reason why its movement in any one direction should be easier than in any other, and the flame surface tends to spread like an expanding soap bubble (see Fig. 4). In a non-spherical combustion chamber, the effect of the walls in checking the free outward surge of unburnt mixture comes into play with unequal effect, and the flame surface tends gradually to assume the contour of the containing walls (see Fig. 5). When the inflammation is in a tube, or in a shallow combustion chamber such as that of an L-head engine, the effect of the walls on the flame becomes apparent almost immediately after ignition.

(5) Movement of the mixture ahead of the flame has a profound influence on its speed. This is exemplified by the effect of the outward surge, due to expansion, of the products of combustion. Similarly, if a stream of an inflammable mixture is ignited, the speed of the flame is increased additively with the speed of the current if it is travelling down-stream (unless the flow is turbulent, when the effect of the speed of the current is more than additive since the area of the flame tends to be increased); whilst if the flame is trying to proceed up-stream, it is possible to render it stationary by suitable adjustment of the speed of the current. The effect of induced turbulence is similar to that of bodily movement of the mixture as a current, and, in addition, the turbulence tends to deform the flame front and increase its area and therefore its linear speed. Too high a degree of turbulence, however, may cause dilution of unburnt mixture with products of combustion, so that the effect of turbulence tends to reach a limit.

Such are the factors which control the initial stages of inflammation in gas-air mixtures. When the inflammation is in a spherical combustion chamber, or in any chamber of which the linear dimensions are closely similar, these are the only factors operating. In asymmetrical combustion chambers, such as tubes or the cylinders of internal combustion engines, further complications may occur due to the effect of resonance set up in the mixture itself. Resonance manifests itself when the inflammation has spread some distance from the igniting source and gives rise to vibrations of the flame front. The result of such vibrations is to increase the area of the flame surface and to augment surge effects, and this tends to be exponential, leading to vibrations of increasing amplitude and a considerably enhanced rate of forward movement of the flame, unless or until the influence of the walls of the combustion chamber checks the effect. Such vibrations may lead to the 'detonation-wave', the sudden greatly enhanced and constant speed of flame movement in which the flame is accompanied by a pressure-wave travelling with the speed of sound under the prevailing conditions; or the inflammability may extinguish itself during a particularly extensive backward vibration. It may be noted that the vibrations of the flame travelling in a tube give rise to an audible note, and that similar vibrations probably invariably precede the 'knock' in a spark-ignition internal combustion engine.

Flame Movement in the Combustion Chambers of Internal Combustion Engines

The observation of flame speed and flame movement in the cylinders of internal combustion engines has mainly been directed towards the elucidation of the problem of petrol-engine 'knock'. Although a complete explanation of this phenomenon has not been agreed upon, the following information regarding the nature of the combustion

FIG. 6

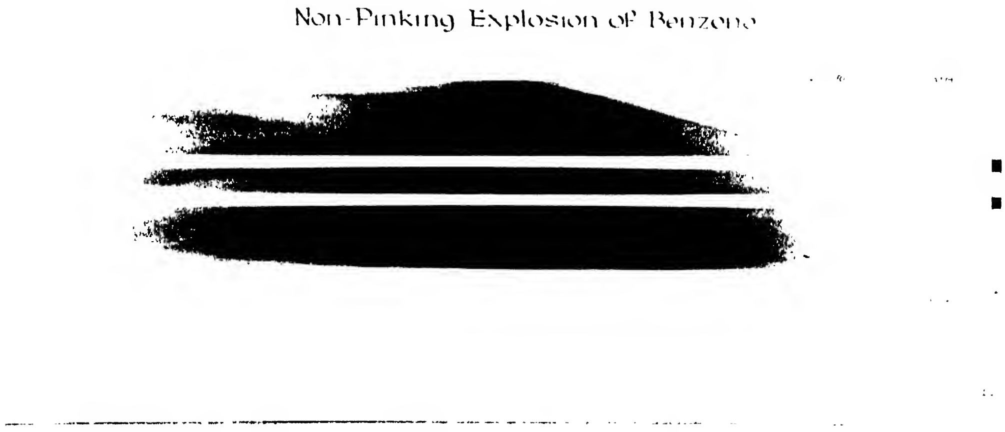


FIG. 7

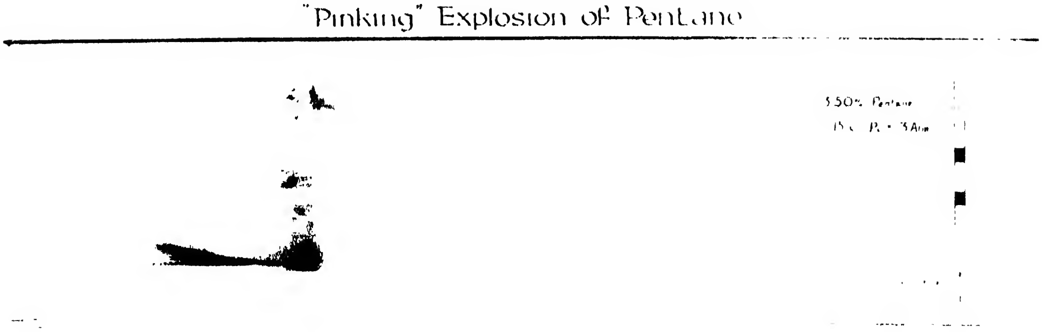


FIG. 8

under knocking and non-knocking conditions has been obtained.

When the inflammation of the substantially homogeneous petrol-air mixture is effected by the passage of the igniting spark, the movement of the flame across the combustion chamber is usually closely similar to its movement in an explosion chamber of constant volume in a laboratory experiment. After a slow start in the more or less stagnant mixture in the plug-body, the flame accelerates until about half the total path to the opposite wall has been traversed, then checks and subsequently travels at a nearly uniform or slightly decreasing speed. The check in the speed of the flame is usually most clearly defined in a vessel of other than spherical form (see Fig. 6). The average speed of the flame is much faster under the turbulent conditions in an engine than in a quiet mixture in a laboratory experiment, but photographic records do not show any marked differences in the character of the flames. Actually, the turbulence induced experimentally by a rapidly revolving fan in a closed explosion chamber frequently alters the manner in which the flame spreads to a greater extent than does the turbulence in the combustion chamber of a side-valve engine.

The subsequent course of events depends on circumstances. During a non-knocking explosion in an engine, or during an inaudible explosion in an experimental explosion chamber, the movement of the flame after its 'arrest' is usually nearly uniform or at a slightly decreasing speed until the end of inflammation. In knocking explosions, the flame front begins to vibrate and then suddenly accelerates after about three-quarters to seven-eighths of the total path have been traversed. Sometimes, but not invariably, ignition of unburnt mixture ahead of the flame precedes or is synchronous with this sudden acceleration; always there is evidence of flame vibration slightly before the rapid acceleration, and photographic records invariably show evidence of pressure-waves traversing the combustion chamber and producing stationary waves. At or about the moment when the sudden acceleration of the flame occurs, a reillumination or 'after-glow' flashes back from the flame front with the speed of sound through the burnt products, and, if a pressure indicator be fitted to the combustion chamber, there is evidence that a pressure-pulse or shock-wave accompanies this after-glow (and may be the cause of it) (see Fig. 8). The impingement of this shock-wave on the walls of the combustion chamber and on the crown of the piston sets up vibration in the metal, giving an audible note or 'knock'.

Photographic records of knocking and non-knocking explosions indicate that one of the main differences between the two is the degree of completeness of combustion in the flame front. Knocking fuels give a very 'thin' flame front and a pronounced recrudescence of illumination when the shock-wave is sent back at the moment of acceleration of the flame towards the end of its travel. With non-knocking fuels, such as benzole, there is a continuous zone of combustion behind the flame front, and, even though in certain circumstances acceleration of the flame is observed towards the end of its travel, there appears to be insufficient residual energy in the burnt products to sustain the pressure-pulse sent back and to develop a real shock-wave (see Fig. 7).

As mentioned previously, observations have been frequently made during knocking explosions, particularly in engine combustion chambers, of an ignition of the unburnt mixture at some point or zone well ahead of the flame. One view of the cause of knock is that the shock wave is due to sudden ignition of an appreciable volume of mixture ahead of the flame, by compression and radiation. This view is not in accord with the observation that such self-ignition is seldom noticed during knocking, even in engine cylinders, though it is certainly more likely to occur in such circumstances than in laboratory experiments, owing to the presence in an engine of 'hot spots' presented by exhaust valves and glowing carbon. Further, it is known that dual ignition in an engine reduces knock, yet common sense and photographic evidence indicate that the unburnt mixture between the two advancing flames will be at a higher mean temperature than when the unburnt mixture is merely compressed against the wall of the combustion chamber. Admittedly, however, with dual ignition the time available for the pre-flame reactions to accelerate to inflammation is reduced. It should be noted, also, that, in an explosion chamber of constant volume, ignition ahead of the flame has frequently been observed with aromatic blends of good anti-knock quality; further, that compression-ignition does not as a rule give rise to shock-waves. The various theories of the cause of knocking are, however, discussed elsewhere in this work. Having called attention to the differences in the character of the flame movements in knocking and non-knocking explosions, a brief reference may be made to the behaviour of anti-knock compounds such as lead tetraethyl.

Lead tetraethyl in the form of undecomposed vapour increases the violence of knock in explosions in a chamber of constant volume. If it is decomposed, however, before it is added to a fuel-air mixture which normally produces a knocking explosion, the combustion much more closely resembles that of a non-knocking fuel, for the combustion initiated in the flame front continues behind it and the whole contents of the combustion chamber are glowing when the flame reaches the end distant from the source of ignition. In an engine the lead tetraethyl is mostly decomposed during the compression stroke, and will certainly be completely decomposed before the initial inflammation has spread any distance from the sparking-plug.

Inflammation in Fuel Sprays

In the spark-ignition Hesselman engine the ignition must depend on the intensity and size of the electric spark and the concentration of fuel droplets and fuel vapour in the path of the spark. The subsequent spread of the inflammation will be determined by the same factors as operate with homogeneous mixtures (i.e. the nature of the fuel, the motion of the air and the fuel, the flame temperature, and the liability of loss of heat). Instead, however, of the reaction velocity being determined, for a given set of temperature conditions, by the strength of the fuel-air mixture, the size and distribution of the fuel droplets will play the principal part in determining the 'reaction-velocity' component of the flame speed. In general, this component will increase as the concentration, fineness of atomization, and uniformity of distribution of the droplets increase. Thus the 'reaction-velocity' component of the flame speed will tend to increase as the load on the engine (and thus the amount of fuel injected) increases. This effect will be magnified by the higher air temperatures at increased loads.

In the compression-ignition engine there tends to be a more pronounced delay period between the injection of the fuel and its ignition, this delay being determined by the temperature of the air and the character of the fuel. With spark-ignition the intense heat of the spark gives almost instantaneous ignition, though the initial slow spread of flame in the stagnant mixture in the plug body gives rise to an appreciable delay period as measured by the most sensitive indicators. In the compression-ignition engine, ignition ultimately probably occurs at some point or zone near the axis of the cone of spray along which the air is carried by the momentum of the spray, so that the relative motion between fuel droplets and the air is small. The flame so initiated will tend to strike back through the fuel spray, if injection is still proceeding, and subsequently to continue like a burner flame until injection ceases. Inflammation now continues during a further period determined mainly by the size of the fuel droplets and the facility accorded them for coming into contact with sufficient oxygen for complete combustion. In an overloaded engine, inflammation is still proceeding when the exhaust valve opens, so that flame and smoke are emitted into the exhaust pipe.

SELECTED BIBLIOGRAPHY

Genera.

Bone, W. A., and Townend, D. T. A. *Flame and Combustion in Gases.* London, 1927.

Ignition.

Morgan, J. D. *Electric Spark Ignition.* London, 1920.
Rothrock, A. M. *J.S.A.E.* **34**, 203 (1934).
Stansfield, R., and Le Mesurier, L. J. *J.I.P.T.* **19**, 287 (1931).

The Movement of Flame.

Ellis, O. C. de C. *Fuel*, **7**, 195 et seq. (1928).
Marvin, C. F. *J.S.A.E.* **35**, 391 (1934).
Maxwell, G. B., and Wheeler, R. V. *J. I.P.T.* **14**, 175 (1928).
Withrow, L., and Boyd, T. A. *Ind. Eng. Chem.* **23**, 539 (1931).
Withrow, L., and Rassweiler, G. M. *Auto. Eng.* **24**, 281 (1934).

FLAME PROPAGATION AND DETONATION

8. FLAME PROPAGATION, PARTICULARLY WITH REFERENCE TO VIBRATORY AND TRUE DETONATION FLAMES

By R. P. FRASER, A.R.C.S., D.I.C.

Imperial College of Science and Technology

Introduction

An explosion being a complex interconversion of several forms of energy occurring at a relatively great rate, a proper understanding of what occurs during the small fraction of time in which the liberation of energy occurs, and the determination of the physical and chemical conditions before, after, and even during the explosion time, is of the utmost importance. Of these, the factors controlling flame movement during explosion, and the new conditions arising therefrom, are perhaps of the greatest interest and value, for it is by their determination that we are able to utilize the greatest force for whatever purpose required.

General Survey

If the proportion of combustible gas or vapour in a mixture with air or oxygen be increased, a point is reached when flame will be propagated throughout the mixture without the necessity of continued ignition. An inflammable or explosive mixture may thus be defined as one through which a flame can be propagated indefinitely independent of, and away from, the original source of ignition. Inflammability is therefore a property of the mixture itself dependent on its composition, temperature, and pressure, and generally independent of the vessel containing it.

For any particular combustible gas and air or oxygen mixture there are, under given physical conditions, certain limits of composition within which self-propagation of flame will take place. These limits defined in terms of the percentage of combustible gas are referred to as the lower and higher limits of inflammability. For a particular gas they vary with:

(1) Position and intensity of the source of ignition.
(2) Direction of propagation, i.e. upward, downward, or horizontal.
(3) Diameter of the vessel.
(4) Temperature.
(5) Pressure.

Stages of Flame Propagation

When a gaseous explosive mixture is homogeneous and stationary, the flame moves through it in a manner and at a velocity determined by a variety of circumstances, each successive burning layer of gas igniting the next one, so that the flame progress is continued so long as any of the explosive medium remains unburnt.

It was first recognized that gaseous explosions pass through certain reasonably well-defined stages by the early investigations of Mallard and Le Chatelier [16, 1883]. They found that when a quiescent mixture is ignited near the open end of a tube a comparatively slow uniform flame was first observed, followed by a period of vibratory motion, and that subsequently, provided the tube was long enough, the detonation wave at another high uniform velocity was set up. This later stage had been recognized and determined by the earlier investigations of Berthelot and Vieille in 1881. Mallard and Le Chatelier further showed that when the mixture was ignited near the closed end of a narrow tube the flame had only a very short period of uniform motion (or nearly uniform motion) and was continuously accelerated without the intervention of the oscillatory period up to detonation.

It may here be mentioned that these observations of Mallard and Le Chatelier were made with combustible mixtures of CS_2+6NO and CS_2+3O_2 having a relatively high rate of burning, and that with mixtures of lower rates or heat content detonation would not necessarily ensue, nor would propagation in the second case be continuously accelerated without the development of an oscillatory period.

The stages of flame propagation in tubes now recognized are

1. The initial stage or uniform motion.
2. The vibratory stage.
3. The pre-detonation stage.
4. The detonation stage.

The first two stages may also be classed as flames travelling below the velocity of sound, and in the last two stages as flames travelling above the velocity of sound.

Although these stated stages of explosion are useful headings, it is difficult to determine when one stage merges into another or where the mode of burning of the earlier stages in an explosion changes to another. Generally speaking, it is considered that during the first stages burning is mainly by conduction of heat from layer to layer, whereas in the last stage of maximum rate of burning it is mainly by adiabatic compression, the flame becoming a compression wave. It is evident from recent work that during all these stages the flame can be greatly influenced by abrupt changes of pressure in the burning layers, such as by means of a compression wave, and that almost all gaseous explosions are complicated by such waves.

The Influence of Vessel Form

It is necessary in studying explosions to appreciate fully both the influence of the form of the vessel and whether open or closed and also the type and position of the igniting source. For these factors profoundly influence the resulting course of an explosion both as regards the flame velocity attained and the total time involved.

All vessels can be said to fall between two limiting forms: on the one hand a sphere, and on the other a long narrow tube.

An explosion of the same mixture (provided it is not a limit mixture) in these two dissimilar forms of vessel will proceed in a different manner. Generally speaking, the pre-detonation, and detonation stages are more likely to develop in tubular vessels where the ratio of length/diameter is large, than in spherical vessels where, as far as is known, these later stages will not appear. Vibratory motions, however, may be observed immediately the dimensions of the vessel become unequal and the effects of pressure waves and flame oscillations become more influential and violent as the ratio of length/diameter becomes greater. It may be mentioned that as this ratio is increased, so the surface-volume ratio will be increased, and effects due to the cooling walls during the early stages of propagation will have greater influence.

Gaseous explosions can never be free from hydrodynamic disturbances set up in the medium by the flame itself. These disturbances will produce mass movements of gas in the vessel and affect the concentrations of the active gases in the flame envelope. Such effects will be much greater when the explosion takes place under conditions of constant volume than they will be under conditions approximating to constant pressure.

The velocity of this mass movement of the gases, when in the same direction, must be added to that of the flame envelope itself to account for the observed velocity. The mass movement will be least in the case of a free unenclosed explosive medium (i.e. a bubble), in which case it is merely the rate of expansion of the gases inside the envelope; and greatest when the confining vessel is closed and far from spherical. Any alteration in mass movement of the burnt or unburnt gases will therefore alter the observed speed of the flame. Such alterations may occur many times during the passage of a flame through a vessel of cylindrical form closed at both ends, particularly if the diameter is small in comparison with the length.

In addition to the pressure disturbances just described, it is now established that a proportion of the energy of an explosion can exhibit itself in the form of compression waves developed by the combustion itself. These waves are produced at an early stage during the travel of flame through the vessel, and if it is closed are reflected backwards and forwards many times. In their passage through the burning gases they momentarily raise the pressure in their path, producing thereby increased luminescence and combustion. Further, should the vessel be tubular and long enough, these compression waves are found to be responsible for the early development and eventual setting up of detonation.

The uneven distribution of pressure in different parts of the vessel as the flame proceeds to fill it, together with the disturbing effects of these compression waves, are therefore found to be extremely influential during the development of an explosion.

The Methods used in the Investigation of Flame Propagation in Explosions

There are two principal methods used for the determination of flame velocities: (1) the electrical method, and (2) the photographic method. The principles of both were devised by the early investigators in this subject, namely, Mallard and Le Chatelier [16, 1883]. Although the same principles are used to-day, their refinement and accuracy have been considerably developed.

The Electrical Method.

This method, which is now only used when photography is impossible, consists briefly in measuring the time between either the fusing of wire bridges or the breakdown of a potential between electrodes placed in the tube at intervals by the flame. In short tubes the method is limited to the measurement of slow flames by reason of inertia and electrical delays. Moreover, it can only record the average velocity between one or more points in the tube and is entirely inadequate with any phase of propagation other than the initial uniform motion. In very long tubes however, the electrical-bridge method was used by H. B. Dixon with considerable success.

The Photographic Methods.

The means for obtaining photographic records may be divided into two groups: (*a*) those using the direct light of the explosion, and (*b*) those using indirect transmitted light from an external source. The records of each group may be obtained in two ways: either as a continuous record taken upon a moving plate or film, or as an instantaneous snapshot obtained upon a stationary negative by the use of either a high-speed shutter or the flash of an electric spark.

(*a*) **Photographs by the Direct Light of the Explosion.** There is no doubt that whenever the actinic qualities of a flame permit, this method is preferable to any other because it enables not only flame speeds to be measured with accuracy but also the whole flame movement to be studied visually.

Graphical Records. By this method a continuous record is obtained by focusing the image of the flame, moving horizontally, upon a film moving vertically at a known constant speed. In this manner a graph compounded from the velocity of the flame image and the velocity of the film is obtained. From this graph, the film velocity being known, the flame velocity can be calculated (Fig. 1). It will be understood that such a photograph allows both a determination of any uniform speed or speeds of the flame, and also an analysis of any sudden changes in speed, such accelerations or retardations portraying themselves on the picture as

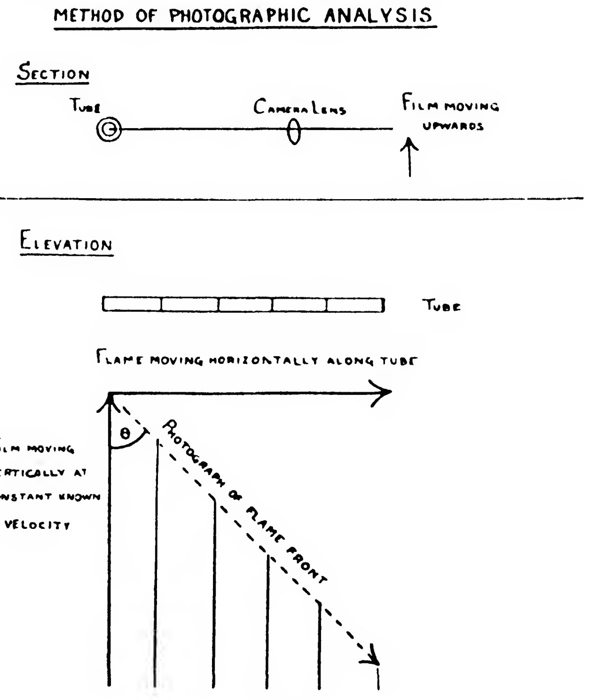


FIG. 1.

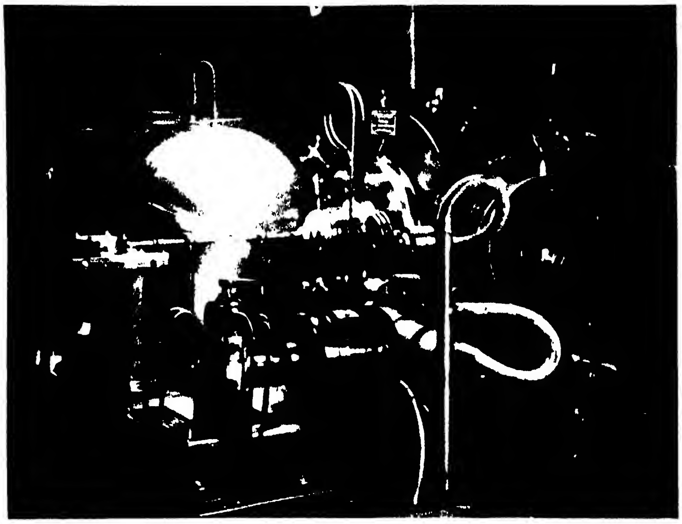


FIG. 2. Fraser high-speed mirror camera

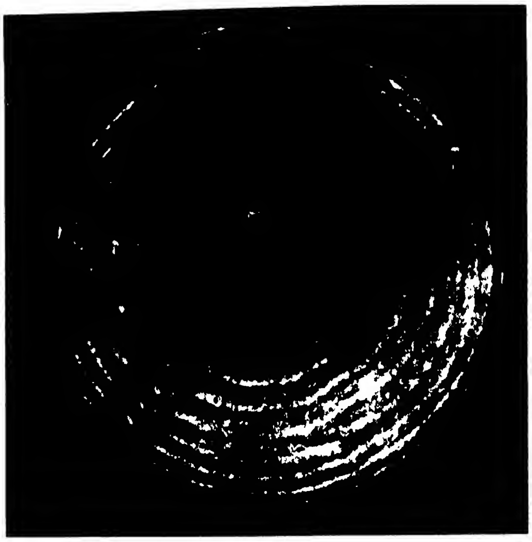


FIG. 4. Flame centrally ignited in a mixture of $10CO + O_2$ in a sphere 9 cm. in diameter, photographed every 2·05 milli-sec. (Ellis)

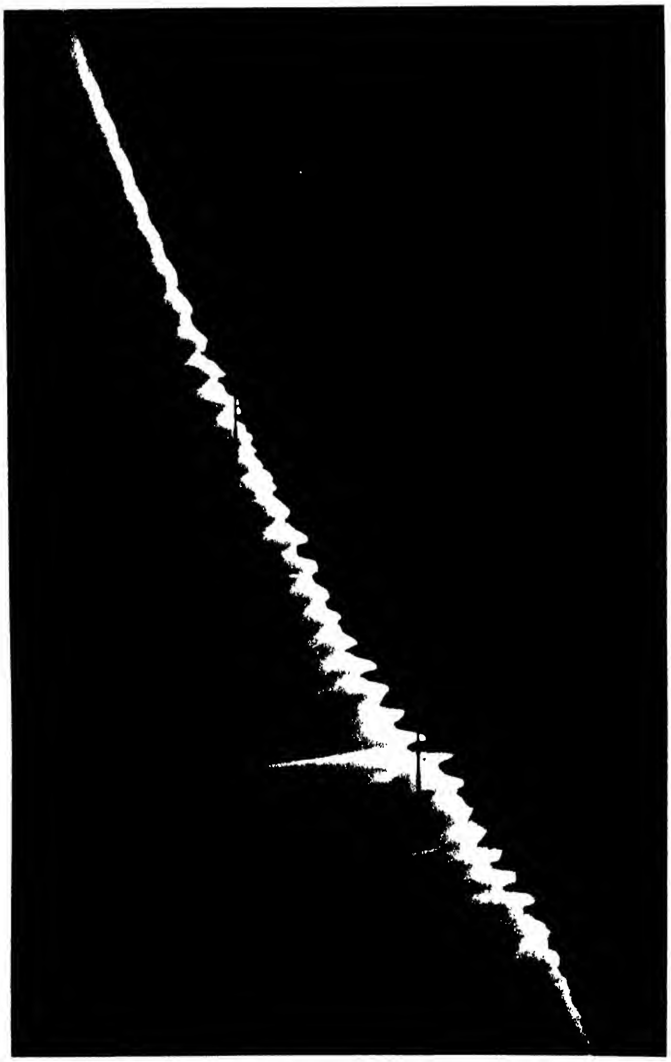


FIG. 8. A graphical picture of the vibrational period in a mixture of $2CO + O_2$ ignited passively at the open mouth of a tube 1·6 m. long. Frequency of vibration 78, 90, 102 per sec. Film speed = x (Fraser). (x = 0·48 m. per sec.)

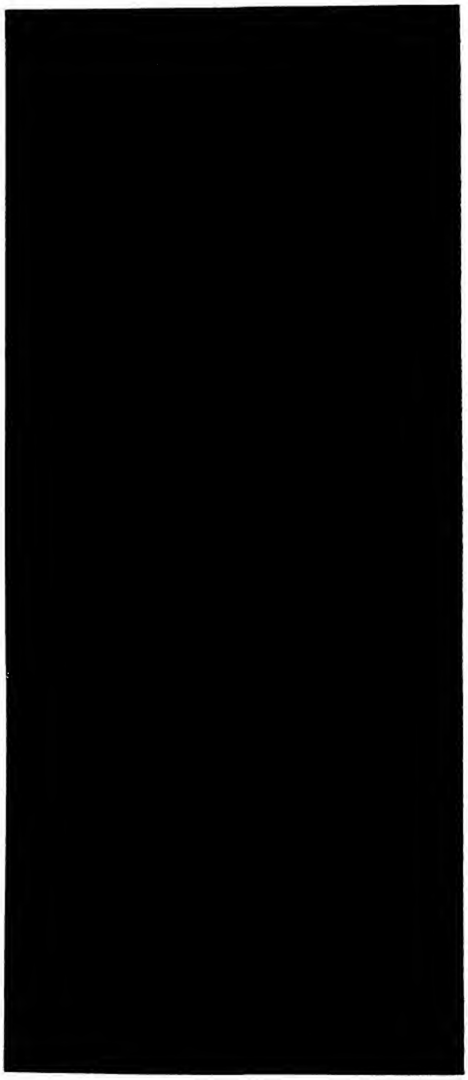


FIG. 9. A graphical picture of oscillatory flame-motions in a mixture of $2CO + O_2$ in an open tube 6·0 m. long ignited passively at the open end

curves of the flame boundary. Furthermore, any difference in the intensity of combustion, giving rise to variations in the luminosity of different layers in the burning masses, will appear as relatively light or dark lines. Movements of these layers either backward or forward horizontally will be discerned in the photograph as lines crossing the picture at angles corresponding to their respective velocities. So also the passage of a compression wave through the flame, by increasing the luminosity of the gases in its path, will appear as a relatively bright line crossing the picture, in consequence of which its velocity and direction may also be determined.

This method of recording can be used equally well both for the slowest and fastest explosions, and, in fact, with the fastest machines is capable of recording flame variations occurring in a millionth of a second. It may here be convenient to describe briefly the latest type of photographic machine for obtaining such graphical pictures.

The Fraser High-speed Mirror-Camera. For successful analysis and the greatest accuracy in determining the velocity of explosions, it is required that the negative be moving at such a speed that the angle subtended by the flame on the photograph be nearly 45°. It is imperative therefore that a camera for this purpose be capable of both very high and wide variation of film speed.

The early apparatus of this type utilized a plate falling behind a lens at the instant of the explosion. The production of celluloid film led to an increase in film velocity obtained by wrapping the film upon a rotating drum. H. B. Dixon [10, 1903] rotated a drum up to a speed equivalent to 50 to 80 metres of film past the lens per sec. This enabled him to analyse and measure the velocity of detonating flames. More recently Fraser [13, 1929] designed cameras with rotating drums giving film velocities up to 200 metres per sec., which speed was found to be the practical limit owing to the effects of centrifugal force and windage upon the film. In 1931 the Fraser mirror camera was constructed (Fig. 2). It employs a different principle to obtain its speed, and has perhaps the highest analysing power available to-day. In this machine the film is held stationary and the image of the flame is rotated by a double-sided steel mirror placed at approximately half the focal distance of the lens (Fig. 3). Two semicircles of film are suspended within a circular casing, upon the circumference of which the lens is fixed. The mirror is rotated at the centre of the circle formed by the films so as to throw the image from the lens upon them. By this means it will be seen (1) the image of the flame in a horizontal tube is rotated at right angles to the direction of flame travel, (2) each side of the mirror in turn rotates the image, (3) the image rotates at twice the speed of the mirror. Rotating the mirror at its maximum speed, 30,000 r.p.m., is equivalent to 60,000 image rotations per minute, which in this machine is equivalent to a vertical film speed of 1,000 metres per sec. To obtain such high speeds of rotation it is necessary to evacuate the camera casing to avoid all windage. With these high equivalent film velocities it is possible to measure with an accuracy of 0·3% velocities of detonations up to 10,000 metres per sec. (i.e. the highest speeds attained by solid explosives).

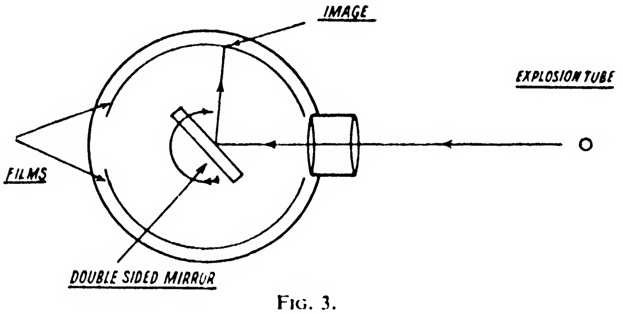


FIG. 3.

Flame Snapshots. These photographs are true pictures of the flame taken in a cinematic manner by means of a shutter device formed either by a periodic coincidence of holes in two rotating disks (Ellis [12, 1928]) or by means of a series of rotating mirrors (Fraser [13, 1934]). The direct snapshot method is more particularly useful for the photography of explosions in small vessels and cannot be used upon flames of high velocity owing to the extreme shutter speeds required for such flames.

(*b*) **Photographs by Transmitted Light.** Photographs by this method can be of two types, and are known as (1) direct shadow photographs, or (2) Schlieren photos.

Both types depend for their success upon the deviation in a ray of light consequent upon any variation in the refractive index of a portion of the gaseous medium through which it passes.

The first type, based upon a method devised by Dvorak in 1880, uses a point source of light to cast a direct 'shadow' of any pressure disturbance upon a screen or photographic plate. This method has been used by many investigators for the photography of moving projectiles and also of sound waves.

Usually a large condenser discharge is utilized as the light source, and various arrangements have to be applied to obtain the spark flash at the desired instant. When the objects to be recorded are compression waves or solid projectiles the method presents little difficulty, but where a luminous explosion or explosion wave is to be photographed it is clear that unless special precautions are taken the light from the explosion will fog the plate and make the result valueless. For this reason, until recently snapshot shadow-photographs of the detonation wave or luminous flames have not been obtainable with much success. A method now being worked out by Fraser and Wheeler, however, has led to some success, and it has been found possible, for instance, to record the form and pressure distribution in the 'spinning' detonation-wave, referred to later.

The second type or Schlieren photographs are based upon a method devised by Topler in [21, 1867], and employed by Cranz [9, 1923], and Payman [18, 1926]. Light from a source falls on a concave mirror and is reflected as a convergent beam. This beam is brought to a focus on the front of a camera lens, and there forms an inverted image of the source. The front surface of this lens is half covered by a semicircular diaphragm. The image of the source is arranged to fall for the most part on this diaphragm, the remainder falling on the lens and forming on the plate or screen an illuminated circle of the concave mirror. A disturbance to be observed is produced in the converging beam between the mirror and the camera lens, the camera lens being focused upon the principal plane of the disturbance. Rays of light which are refracted by the disturbance are bent, and as they converge to form a secondary image of the source at a point removed from the opaque diaphragm they will be diverging again when they reach the diaphragm, and some of the rays which originally fell on the diaphragm will now fall on the lens. Similarly, other rays which passed through the lens now fall on the diaphragm. It will be seen that the rays which now fall on the lens will form a bright line on the plate, whereas rays which are bent so as to fall on the diaphragm will appear as an area of shadow on the plate. The only necessary condition for this process is that there should be a sudden change in density at the surface of the disturbance. In this way the Schlieren principle makes visible a shock wave or an area of heated gas.

A 'wave speed' camera developed by Payman and Shepherd [18, 1926] employs this method in conjunction with the rotating film, so that photographs of explosion phenomena can be taken which show the relative positions of compression waves, flames, and hot products, and as the records are graphical representations, their speeds can be calculated.

The Initial Uniform Motion of Flame through Stagnant Mixtures

The initial slow uniform movement of flame which is observed when an explosive medium is passively ignited at the open end of a tube is found to be independent of the material composing the walls of the tube, but it may be retarded by the cooling influences of the walls unless a certain limiting diameter is exceeded; and, in fact, in very small tubes the flame may be extinguished. This limiting diameter will vary with the composition of the explosive mixture and also with the velocity of flame through it. In other words, the diameter of a tube required to extinguish the flame is smaller the greater the flame velocity.

The distance that the flame will move uniformly in a given case is found to be largely dependent upon both the total length and diameter of the tube. For instance, with a mixture of CS_2+2NO in a tube 2 metres long and 3 cm. diam., the distance traversed uniformly was 0·8 metre, whereas in a tube of the same length 1 cm. diam. it was only 0·25 metre. Increasing the length of tube to 3 metres in the first case increased the length of the period to 1·0 metre.

In spherical vessels or vessels of almost equal dimensions, propagation of flame occurs initially at a uniform speed in all directions. The flame is formed as concentric spherical surfaces as it spreads, and the observed speed will be compounded mainly from the rate of heat-conduction and rate of expansion of the hot gases within the flame envelope. A time will arrive, however, when the expansion within the flame sphere and the concomitant pressure gradient ahead of the flame will have built up a compressed layer of unburnt gas near the walls of the combustion chamber, with the result that an alteration in the speed of spread of the flame, dependent on circumstances, will occur as it approaches the walls. The distance travelled uniformly will depend upon the rapidity of burning and the diameter of the sphere. Fig. 4 illustrates the travel of flame through a slow-burning mixture of carbon monoxide and air in a sphere 9 cm. diameter ignited centrally. It shows the flame spreading more slowly as it approaches the wall of the sphere.

Mallard and Le Chatelier regarded the phase of uniform propagation as being governed by the transference of heat from layer to layer by conduction. From such a point of view the speed would depend only on the composition of the mixture and its temperature and pressure. Regarding the limit condition, Le Chatelier propounded a general rule for calculating the limit of inflammability of a complex mixture of different combustible gases with air. This rule may be written as follows: Let A, B, and C be the simple constituents of an inflammable gas (e.g. Town's gas) and let L_A, L_B, L_C be their limits of inflammability. If the complex limit mixture contains $a\%$ of A, $b\%$ of B, and $c\%$ of C, then the limit for the complex mixture will be

$$L = \frac{a+b+c}{(a/L_A)+(b/L_B)+(c/L_c)}.$$

This additive rule involves the assumption that the admixture of one limit mixture with another of the same type (i.e. lower or higher limit mixture) does not affect the burning or propagation as a whole.

Payman and Wheeler [19, 1922], and later A. G. White [22, 1922], exhaustively tested this rule and found that in most cases a fair approximation to the value of the limit of a binary mixture can be obtained by its application both for vapour-air and gas-air mixtures. Payman and Wheeler attempted to apply the rule more generally. They stated that it held good, not only for limit mixtures but for all mixtures of inflammable gas with air or oxygen, provided that mixtures of the individual gases are of the same type.

Bone, Fraser, and Winter [4, 1927] found considerable divergence from this empirical rule when it is applied to mixtures of gases with oxygen or to mixtures with either air or oxygen removed from the limits. They concluded that the rule is not generally applicable to gaseous explosions and that it cannot be vested with the authority of a natural law. They further concluded that a uniform movement of flame was not necessarily developed in all quiescent explosive mixtures fired at the end of a horizontal tube, and also that only in set circumstances was such a uniform velocity quite the same in all cases. Moreover, it was shown that a uniform movement could be established almost at any stage up to the setting up of detonation under particular circumstances. It can be said that the Le Chatelier rule may have some practical value when applied to limit mixtures of similar gases such that the oxygen concentration would remain almost unaltered, but should be applied only with caution outside such limitation.

Measurements of uniform flame speeds between the limits of inflammability are usually given as speed percentage curves. These curves are useful comparisons of the relative inflammability of different combustible mixtures. Fig. 5 shows a typical series of such curves with gas-air mixtures. The great difference between the limiting mixtures and flame speeds of different gases of such dissimilar character as CO, H_2, and C_2H_2 should be noted. Fig. 6 shows similar curves of some of the gases of the paraffin series with air. It should be noticed that with these gases having similar modes of burning and physical character, that the curves are similar in shape, and that the maximum speeds are all approximately the same except for methane, but that the limits approach each other as the complexity of the molecule increases, as would be expected. It will also be noticed that the limiting speed of all such measurements is approximately 20 cm. per sec. With oxygen mixtures the uniform speeds are much higher, running into thousands of cms. per sec. with such gases as H_2, C_2H_2, C_2H_4 Fig. 7. Generally speaking, the measurement of flame speeds under standard laboratory conditions (i.e. usually in a 1-in. diameter tube of considerable length in proportion to diameter, and passive ignition by a flat flame) gives comparative measurements of the flame movement under these conditions only, and although they aid in making theoretical deductions regarding flame behaviour and perhaps probable behaviour in other vessels of similar form,

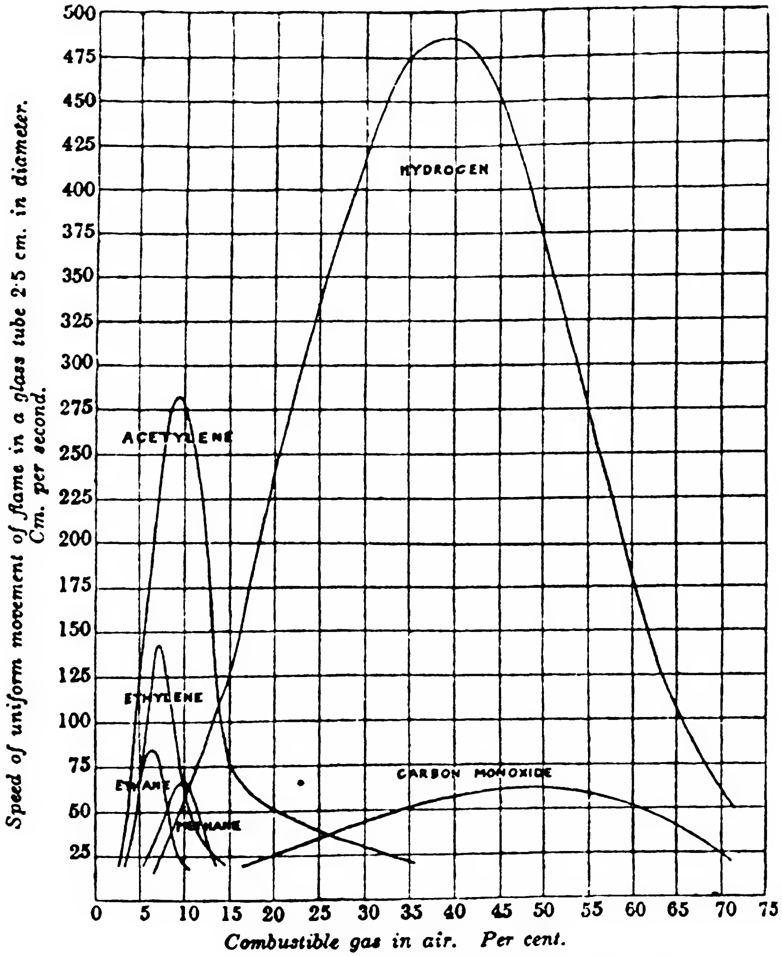


FIG. 5. Comparison of speeds of uniform movement in mixtures of various combustible gases with air (Chapman).

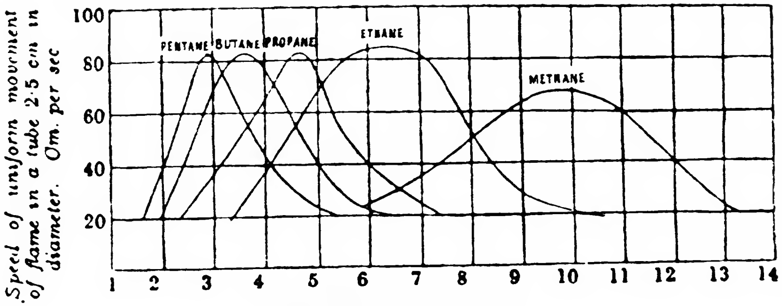


FIG. 6.

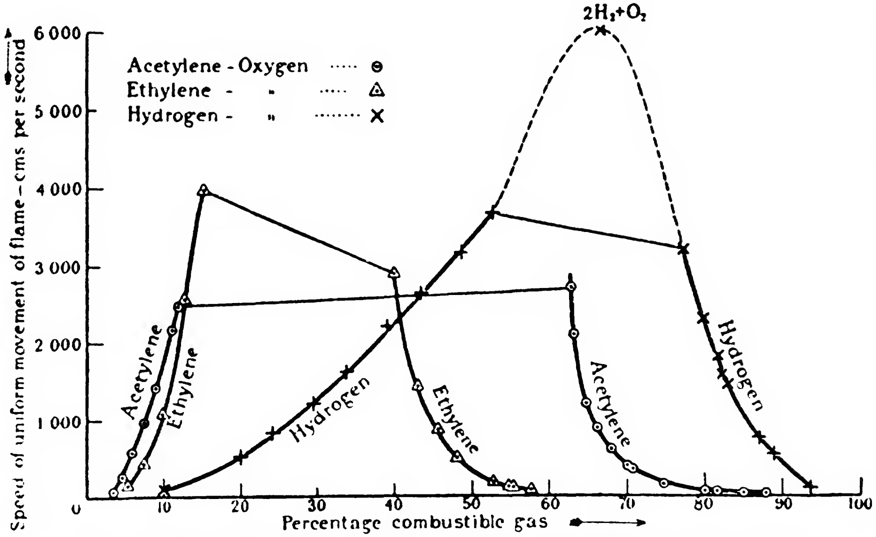


FIG. 7. Speeds of uniform movements of various combustible gases with oxygen (Bone, Fraser, and Winter).

it is difficult to decide when the confining influences of the standard tube become important. Such influences cannot be the same with different gas mixtures having different rates of burning. Nor can the flame surface and the conditions of pressure in it remain inactive as the flame moves farther and farther from the mouth of the tube. It is such changing conditions, largely out of control, which are the limiting factors in such measurements; for whereas with slow-burning mixtures generally the conditions at the flame front can remain steady for some considerable time, with fast-burning mixtures they must change almost immediately the flame is in motion, with the result that the confining boundaries and form of the tube are almost wholly responsible for the results obtained. Therefore such measurements, with the exception of very slow-moving flames, however exact, can have little practical value outside the laboratory without considerable modification and study of the altered confining influences of the vessel upon the flame.

The fact that a flame travels uniformly in any particular case is more an indication that a special set of physical conditions exist in the region of the flame than that a particular mode of burning of the gases themselves is being sustained, though it does imply a regular supply of unburnt gas and a uniform rate of reaction.

Oscillatory and Vibratory Movements in Flames

1. Vibratory Motions in Open Tubes.

Mallard and Le Chatelier [16, 1883] recognized that the slow flame-speeds of the initial uniform movement in tubes would be accelerated by turbulence which would assist in the transmission of heat. They named two types of vibrational propagation: *Mouvement saccadé* and *Mouvement vibratoire*. The first they described as periodic accelerations and retardations of the flame of considerable amplitude; the second they described as being limited to the region of the flame front. At least three types of vibratory motions in explosions may now be recognized: (1) those due to the acoustical properties of the vessel; (2) those caused by regions of pressure difference; (3) those resulting from the presence of compression waves.

Each of these types of disturbance may be said to produce a kind of auto-turbulence within the burning medium, so that the average rate of burning is increased.

When an explosive mixture is contained in any vessel open at one end and ignition is effected at this opening, as had already been said, the condition of pressure at the flame surface will change when the flame has moved so far from the opening that the pressure produced by expansion cannot dissipate to the atmosphere. When this position is reached in a tube the flame may *either* with (1) a fast-burning medium accelerate continuously, *or* vibrate and surge backwards and forwards with variable but generally increasing amplitude, or (2) with slow-burning mixtures these variations may not occur, but the flame envelope itself may vibrate by continual alteration of form like a flexible diaphragm. These movements have been shown to be influenced by the acoustical properties of the tube. Mason and Wheeler [17, 1919–20] found that they were the direct result of the resonance of the column of gas lying between the flame front and the closed end of the tube. The frequency of the vibrations agree closely with the frequency calculated for organ pipes of the same dimensions as the portion of the tube remaining ahead of the flame front. Since the flame acquires its motion from the vibratory column of gas ahead of it, the amplitude of the vibration of the flame front increases as the resonance becomes stronger. The period of vibration is therefore varied by the length, diameter, speed of flame, and the position of flame in the tube at any instant.

Fig. 8 shows a typical graphical picture of a uniform motion and subsequent vibrational period in a mixture of $2CO+O_2$ contained in a tube open at one end 2·5 cm. diameter and 1·6 metres long ignited passively at the mouth with a flat flame. The flame is seen to progress uniformly for 0·3 metre at a velocity of 240 cm. per sec.; it then starts to vibrate, at first with a very small amplitude, but becoming greater after a few more cm. run. As it approaches the closed end of the tube it is seen to lose speed, and very rapid vibrations appear in the flame envelope.

In the case of (1) fast-burning mixtures, the acceleration and/or swinging backwards and forwards is found to be mainly due to unequal pressure distribution before and behind the flame, so that it is alternately hindered by expansion in front of it or accelerated by expansion behind it. O. C. de C. Ellis [12, 1928] has shown by snapshot photography that the gas motion produced by these expansions will greatly alter the form of the flame envelope, with the result that the area of the flame surface upon which the rate of burning partly depends will fluctuate exceedingly. This type of oscillation is usually found to be of considerable amplitude, so big, in fact, that in narrow tubes of considerable length the flame may be forced so far back into its own products of combustion that it may be extinguished or alternatively thrust quickly forward so as to initiate detonation earlier. It is found that such oscillations as these will usually cease to occur after the flame front has attained a velocity above the velocity of sound in the mixture. Furthermore, it has also been found that during this phase compression waves are produced by the flame itself. These waves travel ahead of the flame and are reflected from the closed end of the tube.

Fig. 9 is a graphical record showing such oscillatory flame motions in a $2CO+O_2$ mixture contained in an open tube 6 metres long by 1·2 cm. diameter ignited passively at the open end.

The flame is seen to be at first accelerated forward irregularly and then to be alternatively moving forward and backward in the tube. The oscillations are seen to have no uniformity, but considerable amplitude. The compression waves produced by the flame after reflection from the end of the tube make themselves visible as luminous tracks in the burning medium behind the flame front. They are seen to be largely responsible for the sudden retardation of the flame during the later stages depicted in the photograph.

Where ignition is made to occur a short distance inside the mouth of a tube, it is found that no uniform motion will ensue but that an oscillatory motion may be set up immediately.

2. Vibratory Motions in Closed Tubes.

In stagnant mixtures in closed tubes, no matter where the point of ignition is placed, the flame is found to accelerate almost immediately away from it. This initial accelerating movement is followed in all cases by a retardation, so that the flame may remain almost stationary or even suffer a reversal of motion in some cases. It may then advance again in a second stage either almost uniformly as in a slow-burning medium, or in a series of further accelerations and retardations or 'surgings' (Fig. 11).

The first retardation of the flame in such vessels has been

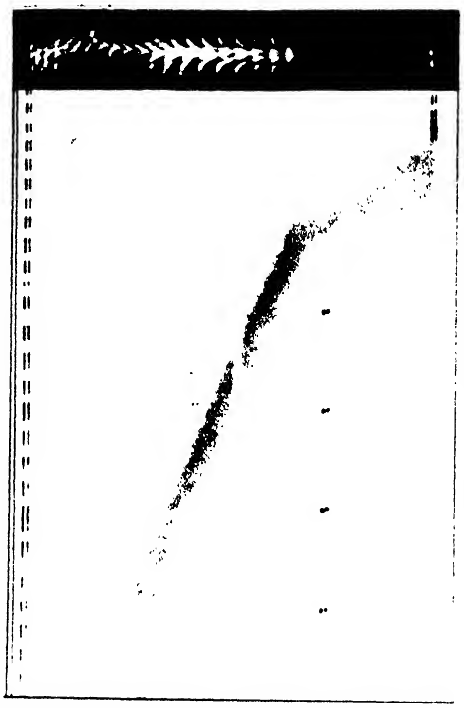


FIG. 10. A series of snapshots and a corresponding graphical photograph of flame in a mixture of $13CO + O_2$ in a closed tube 32 cm. long. (Ellis)

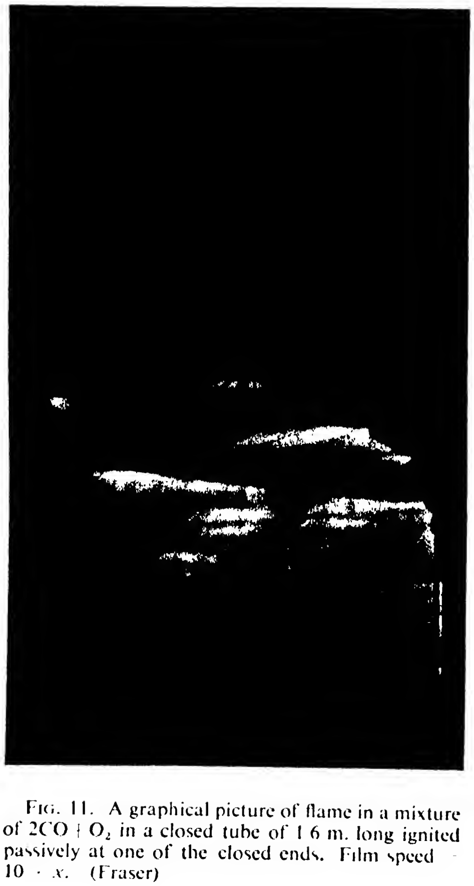


FIG. 11. A graphical picture of flame in a mixture of $2CO + O_2$ in a closed tube of 1·6 m. long ignited passively at one of the closed ends. Film speed = 10 × x. (Fraser)

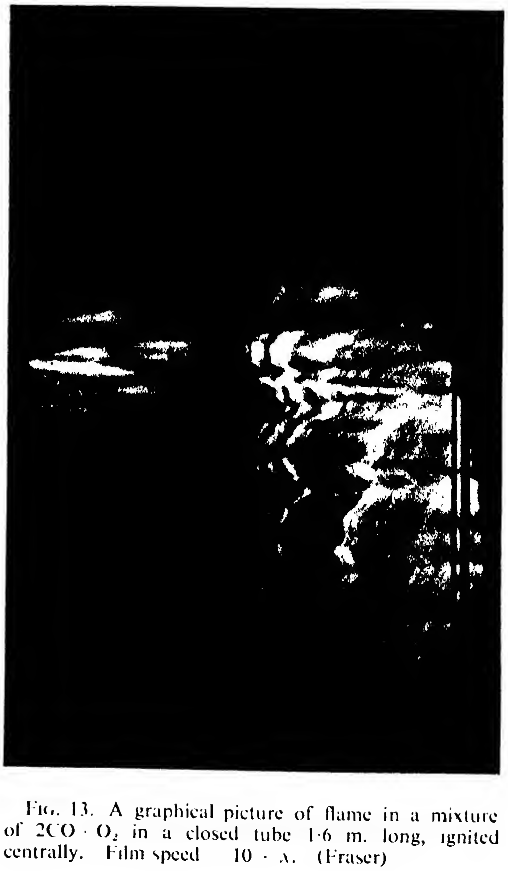


FIG. 13. A graphical picture of flame in a mixture of $2CO + O_2$ in a closed tube 1·6 m. long, ignited centrally. Film speed = 10 × x. (Fraser)

named the 'flame arrest'. Several alternative explanations of the cause of this flame arrest have been advanced. Dixon [11, 1921] thought that it is caused by the compression wave from the spark striking the flame after reflection from the end of the vessel. This view is untenable for many reasons, among which is the fact that the arrest is found in cases where ignition has been perfectly passive, i.e. a pilot flame or hot wire. Woodbury, Lewis, and Canly [23, 1921] thought that it occurred when the pressure of the unburnt gases before the flame front equalled the pressure of the products behind, the pressure ahead of the flame front being built up by reason of its confined movement. Hunn and Brown [15, 1928], as the outcome of experiments on carbon disulphide and oxygen mixtures exploded in an apparatus recording simultaneously the pressures at different positions in the tube during explosion, formed the opinion that it occurred at the instant a large compression wave born behind the flame front overtook the flame. This view, however, is difficult to substantiate in view of the fact that compression waves are known to accelerate flames when overtaking them (Bone and Fraser [1, 1929]). Ellis [12, 1928] analysed many explosions of carbon monoxide and air by means of snapshot photography and came to the conclusion that the initial period of acceleration lasts until the volume of the flame products approximates to half the volume of the tube, provided the tube was not too narrow. Furthermore, that the arrest is produced when the flame alters in shape from an elongated cylindrical solid and makes contact with the walls of the tube, thus allowing a relatively sudden loss of energy behind the flame front to occur. This explanation is probably correct. Fraser [14, 1930] concluded that arrest occurred by reason of the combined influence of cooling of the flame products behind the flame front and pressure built up ahead of the flame leading to rapid local alterations of pressure, causing movement of the gases *en masse* independent of the flame but set up by it.

In slow-burning mixtures, after the 'arrest' the flame may progress almost uniformly to the end of the tube. During this stage the flame envelope is found to have a trumpet-like form with the narrow end away from the direction of travel. A photograph obtained by Ellis illustrates this flame form (Fig. 10). It shows a series of snapshots at intervals of 9·63 millisec. of flame in a mixture of $13CO+O_2$ in a tube 32 cm. long by 4 cm. diameter, and also, for comparison, a related graphical picture of a similar explosion.

The more or less constant speed of the flame developed during the later stages of such an explosion seem to be established owing to a process of pressure stabilization determined by the condition of the environment. With fast-burning mixtures, after the first arrest the flame travels forward again with increased velocity, to be suddenly checked in an even more abrupt manner than during the first arrest. If the tube be long enough, this process is repeated until the flame reaches the end of the vessel.

Fig. 11 is a graphical picture of the explosion of a mixture of $2CO+O_2$ in a tube 1·6 metre long by 2·5 cm. diameter ignited passively at one of the closed ends. It shows the flame accelerating from the point of ignition up to a speed of 60 metres per sec., which then falls to about 30 metres per sec. until at a distance of 32 cm. from the ignition-point it is suddenly checked and reversed in direction. It then travels forward again at a speed of approximately 90 metres per sec. for a further distance of 43 cm., whereupon it is again arrested and its direction momentarily reversed. Subsequently it advances again, to be checked several times before reaching the end of the tube. The total time taken for the flame to travel to the end of the tube was 24·5 millisecs.

3. Compression Waves in Closed-tube Explosions.

In this photograph it should be noted that at the point of the *second arrest* a compression wave is seen to pass through the flame envelope and enter the burning medium, making itself visible by increasing the luminescence of the hot gases in its path. This wave is reflected from the end of the tube back towards the flame front. At the flame front it is partly reflected back again into the *burning medium* and partly transmitted through the *unburnt medium* to the far end of the tube, where it is reflected towards the flame front again (Fig. 12). Upon striking the flame front the flame is suddenly halted as before. It is seen, therefore, that, whereas the first arrest as before stated is due to an initial gas surge, the second and subsequent arrests of a more abrupt nature are due to the passage of a compression wave, continually reflected from the end of the tube, colliding with the flame front.

When the same tube of explosive mixture is fired passively at the centre of the tube, the flame will proceed in both directions towards the ends of the tube. Fig. 13 shows such an explosion. The flame is seen to progress in exactly the same manner in either direction from the point of ignition. A series of 'arrests' occur caused by the same series of events as above described, with the distinction, however, that now two original compression waves are produced, which, upon entering the flame envelope are reflected backwards and forwards within it. The time for the flame to reach the ends of the tube in this case was only 16·2 millisec. compared with the previous 24·5 millisec. for the first example.

The two waves created by this position of ignition initially travelling in opposite directions may coalesce early during the passage of the flame, with the result that later stages of the combustion are influenced by only one compounded wave traversing the tube from end to end. This coincidence of waves increases the displacement of the gases by the wave and decreases the number of wave passages per sec. through the vessel, whereas if the two waves never coalesce, the resultant flame motion is generally faster and the combustion more disturbed and rapid. The passage of compression waves during the early stages of an explosion while the flame envelope is moving through the mixture must necessarily be very complex owing to three main causes: (1) the varying densities of the different areas of unburnt and burning gases; (2) the varying velocities of gas movements due to pressure difference; (3) the fact that any wave may be totally or partially reflected at a flame surface.

The fortuitous production of a single compression wave during the early stage of flame propagation in an explosion will have a great influence upon its further development. Furthermore, extremely small differences in form of the combustion space may greatly influence compression-wave reflections and the course of the explosion.

The mechanism of the production of the initial compression wave in the type of explosion just described is not clear. It may be said, however, that the wave originates at a time just after the initial 'flame arrest' indicated in Fig. 12. In all probability it results from a flame disturbance caused by the same gas movement that produce the first arrest.

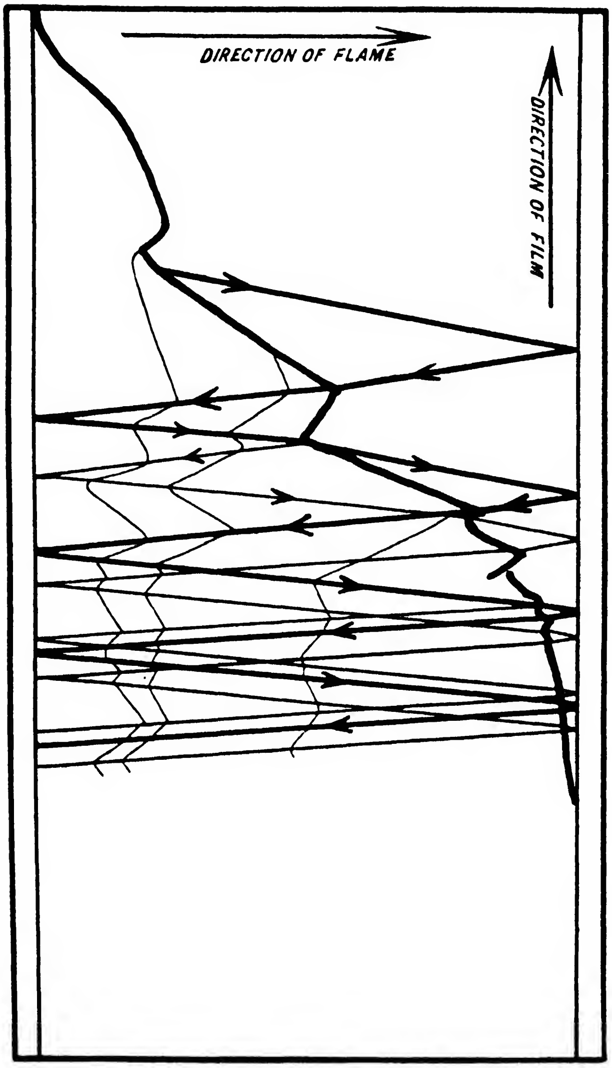


FIG. 12. Diagrammatic representation of Fig. 11 showing the initial compression wave (heavy arrowed line) being reflected from the flame surface producing at first two and subsequently three waves traversing the tube during the later stage of combustion.

The amount of turbulence produced by the passage of these compression waves will depend upon: (1) their number, (2) their velocity, and (3) the length of the vessel. The number of waves surviving will be dependent mainly upon the position of ignition and the shape of the reflecting surfaces within the vessel. The length of the vessel and the wave velocity will control the number of passages through the medium in a given time. The velocity of the wave will be dependent upon its intensity and the temperature and density of the medium.

When a similar explosion to that depicted in Fig. 13 is made to occur in a tube one-quarter the length, i.e. 0·4 metre long (Fig. 14), the later stage of combustion after the flame arrest is disturbed by the much more frequent passage of the two waves obtained by this midway position of ignition. A further analysis of this later stage at a greater film velocity is shown in Fig. 15. This picture represents 1·5 millisec. of the phenomena in a $2CO+O_2+2H_2$ explosion in a closed tube 35 metres long. The two compression waves both having velocities of approximately 1,000 metres per sec. are seen being continually reflected from the ends and crossing in the middle of the tube. The successive displacement of the burning gases backwards and forwards is clearly seen.

4. Explosions in Closed Tubes with Very Fast-burning Mixtures.

Where the explosive mixture is of such a composition that its rate of burning is extremely high, the flame oscillations or 'arrests' just spoken of may not occur. The flame may accelerate immediately up to a velocity much greater than the velocity of sound, eventually approaching that of detonation. Fig. 16 illustrates such a case. The picture shows the explosion of a mixture of two parts of 'knall gas' to which has been added one part of acetylene $2(2CO+O_2)+C_2H_2$ to raise the rate of burning; in a tube 1·6 metres long by 2·5 cm. diameter ignited passively at the centre. The flame is seen to accelerate without change almost to the ends of the tube where detonation ensued. Powerful reflection waves are seen to pass backwards towards the centre from both ends of the tube, the greater part of the combustion taking place in their path, and the tube is instantly shattered.

The Effects of Shock Waves upon Flame Movements up to the Development of Detonation

It has long been known that a column of explosive mixture, confined in a narrow tube of sufficient length *and closed at one end*, detonates more quickly when ignited near the closed end than when ignited at the open end. H. B. Dixon in 1903 advanced the view that this more rapid attainment of detonation was due to a wave from the initiating spark being reflected from the closed end of the tube and overtaking the flame from behind, thereby accelerating it. Experiments by Bone and Fraser [1, 1929] were undertaken to study the effects of mechanically produced shock waves shot at successive intervals into the burning mixture from behind the flame. Both the intensities and time intervals between successive waves were variable and under control.

(*a*) The Effect of Shock Waves upon Flames travelling at a Velocity below that of Sound

In their experiments the mean velocities of the shock waves for the first 50 cm. of travel were found to be between 340 and 420 metres per sec. according to the nature of the spark source producing them.

After a small initial acceleration of the flame a substantially uniform velocity was attained, when it was found that the passage of a shock wave through it caused an immediate change in this velocity to a second and higher almost uniform velocity. A succession of such shock waves, sent into the explosion at a relatively great rate (200–400 per sec.), caused the flame to increase in velocity in a series of successive steps, each of uniform type, until the flame had attained such a speed that no further wave could overtake it. The difference in velocity between two successive stages of uniform motion was found to depend upon the relative velocities of flame and shock wave, and upon the intensity of the shock wave measured in terms of its velocity.

Using more intense waves produced by detonators, a similar sequence of events occurred, but much larger changes in velocity were observed. The velocity of the flame quickly, and sometimes immediately, exceeded the

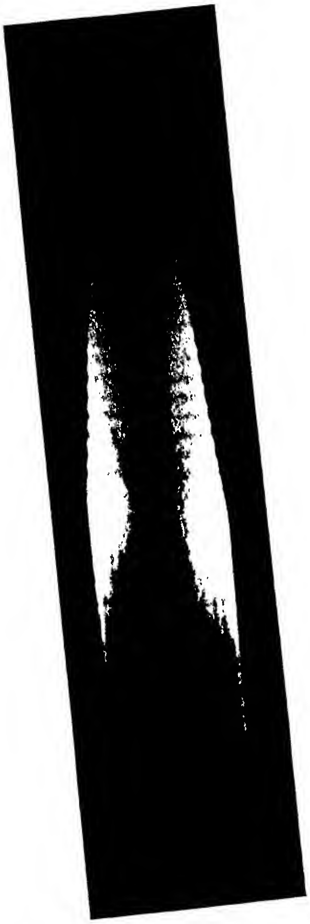


Fig. 14. A graphical picture identical in all respects to Fig 13 except that the tube is one-quarter the length. (Fraser)

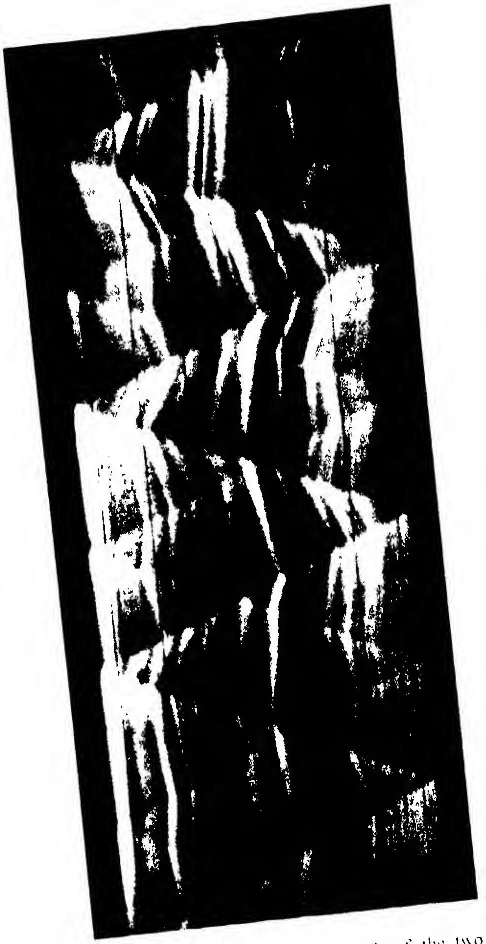


Fig. 15. A higher speed analysis of the two compression waves traversing the tube in the later stages of an explosion similar to Fig 13. (Fraser)

Fig. 16. A graphical picture of an explosion in a tube 1·6 m. long of a fast-burning mixture of $2(2CO + O_2) + C_2H_2$. Film speed $= 40 \times x$. (Fraser)

velocity of sound after being overtaken by one shock wave only, and no further sudden increases were observed other than in the pre-detonation stage.

The fastest and therefore more intense shock waves increased the speed of flame in the greatest ratio; similarly, the greatest increase occurred when the difference in velocity between flame and shock wave was greatest.

The immediate change in the luminosity of a flame front and products behind the front, after the passage of a shock wave, indicates an almost instantaneous rise in pressure in the flame, thereby increasing the temperature and rate of reaction. In other words, the reaction velocity is raised to a new level by reason of which a new and higher forward velocity can be maintained. It should again be emphasized that there is no very fundamental significance about these uniform velocities, as is evidenced by the variety of figures which can be obtained in differing circumstances. In fact, a uniform velocity is rather exceptional than otherwise, indicating a temporary balance in a given set of physical conditions.

(*b*) The Motion of the Gases before Detonation.

Should the rate of burning be such as to allow the escape of pressure behind the flame front, then uniformity may be maintained, but in other cases where burning is more rapid the pressure developed must expend itself by setting the gas in motion in front of the flame envelope as well as behind. There is thus created a pressure gradient ahead of the flame, and the flame burns through already moving gas. Strange as it must at first appear, gas velocities well over the velocity of sound in the medium may be reached, and are measurable in explosion photographs. It must be concluded that this is made possible by the fact that the high-pressure centre which causes the gas to move is never moving *relative to the gas at a velocity greater than that of sound*. As soon as this did happen the gas motion would die away, and there would only remain a very steep pressure gradient just ahead of the flame. Experiments by Campbell and King [7, 1931] have shown that a pressure was discernible as far as 150 cm. ahead of a slow-moving flame starting from a closed end of a tube, while in the case of a $2CO+O_2$ flame travelling at 100 metres per sec., pressure was discernible 75 cm. ahead of it. In the cases of $2CO+O_2$ and $2H_2+O_2$ detonations, no pressure gradient farther than 3·5 cm. ahead of the flame could be detected, and these two examples may be taken as characteristic of the two groups of striated and non-striated detonation photographs, which are referred to later.

(*c*) Flames overtaking Shock Waves.

It is evident that once a flame is moving relative to a combustible medium at a velocity greater than that of sound, it becomes possible for it to overtake a shock wave which may be travelling ahead of it. As has been pointed out, sudden changes in velocity during flame propagation are caused by a shock wave overtaking the flame, and it would be expected that an abrupt change should be produced when the flame overtakes a shock wave. Such is indeed found to be the case, and, in fact, the sudden initiation of detonation in gases is attributable to this cause.

It may often happen, however, that the flame velocity is raised through overtaking a shock wave, but it may not be raised to a sufficiently high level for detonation to be established until a second or third wave is overtaken.

(*d*) Auto-ignition.

It has been observed photographically that the initiation of detonation in a tube is preceded by a condition in the gases ahead of the flame such that auto-ignition in them can occur (Fig. 17). That is to say, burning is suddenly and spontaneously initiated at a point which may be as much as 6 or 7 cm. in front of the main body of flame. Of the two new flame fronts so formed, one travels forward with an increased velocity, while the second new flame travels backward in the tube to meet the original forward-moving flame. At the point where they collide a shock wave is created which moves backwards through the still-burning medium. In those cases where detonation is initiated this has been named the 'retonation wave' on account of its invariable reverse velocity from the point of detonation. It is, in fact, simply a shock wave.

Auto-ignition, when first observed, was thought to be a photographic peculiarity. It is now thought to be caused by the combined influence of pressure and radiation upon the shock wave as it is overtaken by a flame in the pre-detonation stage. Increased pressure is supplied by the superposition of the pressure gradient normally ahead of the flame, upon the pressure of the shock wave (Bone and Fraser [2, 1931] and Campbell and King [7, 1932]. It has been recently suggested that simultaneously with the increase in pressure the radiation from the flame is absorbed by the comparatively dense gas layer constituting the pressure wave, producing ignition thereby (Bone, Fraser, and Wheeler [3, 1935]).

The Detonation Wave.

There can be little doubt that during the initial stages of an explosion the combustion in the flame front is comparatively incomplete and much combustion goes on behind it. In detonation, on the other hand, the chemical change concerned in the wave front occurs practically instantaneously and combustion is almost complete. Should the medium burn in distinct chemical stages, however, only the first stage may actually be concerned in the wave front. Under the extreme conditions of this mode of combustion it appears that successive layers of the explosive mixture are suddenly ignited by the combined action of adiabatic compression and radiation.

Berthelot and Vieille (1881) made the important discovery that each particular explosive mixture had a definite maximum rate of explosion. When propagated at such a maximum velocity they termed the flame the *L'Onde explosive*. They likened it to a sound-wave passing through the medium, with the difference that, whereas a sound-wave is propagated from layer to layer with a small compression, in the detonation wave there is propagated an abrupt change in chemical condition which generates an enormous force as it passes through each successive layer of the medium. About 20 years later this sound-wave theory was modified by Vieille. He regarded it as a special type of shock wave in which an abrupt change of pressure in the vicinity of the wave front is maintained by the adiabatic combustion of the medium through which it is propagated.

Since its discovery it has been generally considered that in the detonation wave chemical change is propagated under the most intense conditions of temperature and pressure and, therefore, with the utmost rapidity; and it seems probable that practically all collisions between oxygen molecules and combustible in the flame front must be fruitful of change; accordingly the flame is highly luminous and of extremely short duration.

For example, the flame velocity in a tube during the initial uniform stage with a mixture of $2CO+O_2$ saturated at 15° C. is about 0·3 metre per sec., whereas its detonation velocity is 1,760 metres per sec. under the same conditions. Similarly, a 3% pentane-air mixture has an initial flame speed of approximately 0·8 metre per sec. and a detonation velocity of 1,780 metres per sec. Combustible gas mixtures with oxygen may have detonation velocities up to *c.* 3,500 metres per sec.

Berthelot concluded that the detonation waves had a constant velocity for the one and the same explosive mixture at a given temperature and pressure which was independent of direction of travel and diameter of tube.

The Spinning Detonation wave.

Prior to the year 1926 investigators had concluded that the wave front in detonation was homogeneous as regards pressure temperature and chemical action. Campbell and Woodhead [8, 1926], in photographing certain detonation flames, discovered the so-called phenomenon of 'spin' and directed attention to the unusual appearance of the graphical photographic record of detonation in a mixture of $2CO+O_2$. The flame edge in this record presented a regular undulatory appearance, but the mean rate of progress of the wave was uniform and characteristic of the explosion wave in this mixture. The apparent propagation was in spurts, each spurt taking place at approximately equal intervals in the tube. The frequency of the undulation in such a photograph was of the order of 45,000 per sec.

The major portion of the luminosity behind the wave front was segregated into bands, each of which appeared to have its origin in one of the undulations of the wave front. The bands appeared to be equally spaced; they were usually straight in some records, but definitely curved in others. They were inclined at a small angle to the horizontal, suggesting a reverse motion at some tens of thousands of metres per sec. Fig. 18 shows such a photograph. It is of the detonation in a $2CO+O_2$ in a tube 13 mm. bore and shows the wave travelling at a constant velocity of 1,760 metres per sec. It shows the undulatory flame edge referred to and also the banded appearance in the luminous gases behind the wave.

Later photographs obtained by Campbell [5, 1928] and contemporaneously by Bone and Fraser [1, 1929] show that the curious banded appearance of the photograph is given by *all* $CO–O_2$ detonations (e.g. $3CO+O_2$, $4CO+O_2$, $CO+O_2$, $2CO+O_2+N_2$) and also by those of the detonation in *certain* mixtures of oxygen and methane, ethane, ethylene, carbon bisulphide, or cyanogen, but *not* by those of hydrogen-oxygen media. Recent work has shown that with hydrogen-oxygen media spin is discernable near the limits, or by those of $2CO+O_2$ when upwards of a small percentage of H_2 (about 10%) is added.

It has now been proved beyond any doubt that the origin of the undulations and striations in the photographs is the rotation of some part of the flame. Other suggested origins, such as periodic motion of the camera, longitudinal vibrations in the tube, transverse vibrations of the tube, and others, have been definitely eliminated. Recently it has been shown, in conformity with the flame rotation theory, that a glass tube silvered on the inside surface shows a keen cut helix after the passage of a $2CO+O_2$ detonation wave. The pitch of the helical track varies with the internal diameter of the tube; the ratio L/D (L = pitch, D = diameter of the tube) remains constant at approximately 3·0. It is probable that other mixtures than $2CO+O_2$ would yield a similar constant ratio, but few other mixtures produce spiral records of such clarity and regularity, and in consequence the large proportion of investigation into this phenomenon has been carried out with carbonic oxide mixtures.

There has been—and there still is in some quarters—some doubt as to exactly what is rotating inside the tube. The problem has partly resolved itself into a question as to whether the whole body of gas in the explosion tube is rotated. The rotational speeds in question are extremely high. The first explosions of this type analysed, namely, $2CO+O_2$, showed that the speed of rotation in a tube 13 mm. bore was 44,000 rev. per sec. More recent experiments with other explosive mixtures have shown rotational speeds as high as *c.* 500,000 rev. per sec. Furthermore, there has still remained the somewhat puzzling banded appearance of the graphical record. The suggestion has been strongly upheld for some time (Campbell and Finch [6, 1928]) that the luminous bands represent a series of instantaneous pictures of a tail or track of the highly luminous 'head', the whole body of luminous gas rotating, producing in effect an extremely rapid shutter action. This would result in a series of dark and light bands in a graphical record. To those who doubted the probability of the gas in the tube rotating at the high speed referred to (Bone and Fraser [2, 1931]) the origin of the bands was admittedly a mystery, and they were unable at the time to put forward any adequate alternative explanation. They maintained that the only helical motion was that of a most intense centre of combustion at the very head of the explosion wave which followed a helical track, through stationary gas, the main burning of the gas originating from this helix.

It will thus be seen that two distinct views of the internal mechanism of the phenomenon were put forward by different schools of thought, neither completely satisfying, but each supported by a considerable body of circumstantial evidence. An attempt was made to calculate the frequency of spin to be expected with a given detonating mixture in a tube of any defined size, by Shtsholkin in 1934 [20]. This calculation was based upon the assumption that the mass of gas moves spirally, and the figures obtained agreed quite well with those obtained experimentally. The calculation, however, can be seriously criticized on the grounds that the assumptions made therein, while perfectly legitimate at normal rotation speeds, would probably be completely invalidated by the enormously high speeds encountered in the circumstances considered.

A more complete explanation of the phenomenon has only very recently been formulated by Bone, Fraser, and Wheeler [3, 1935]. It may possibly be criticized on the grounds of insufficient evidence, although as a whole it is quite consistent and well substantiated. In brief, it may be said to support the idea that the head of detonation alone follows a helical track rather than that the body of the gas rotates as a whole.

They suggest that under certain conditions any combustible gas will exhibit spin in detonation, the main condition being that the mixture must be such as to be capable of burning at an increased rate when compressed and excited by radiation; the limit being reached when the molecules just about to be burned are completely excited. It is also suggested that more rapid and thus more intense burning will produce locally more intense radiation, which will have the effect of increasing still further the rate of burning of the gas nearby, up to the limit just named. When a shock wave is being caught by a flame it may become ignited when the flame is still some distance behind

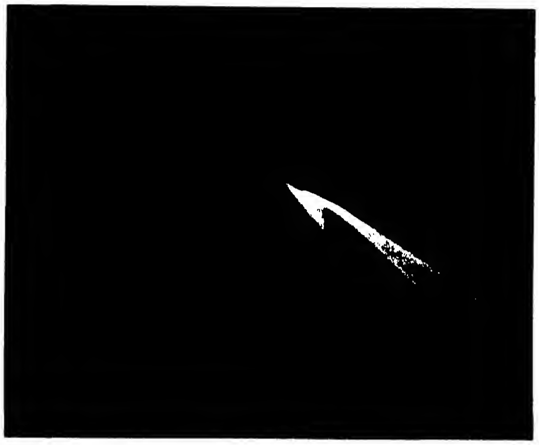


FIG. 17. Auto-ignition in a mixture of $2CO + O_2$ in a tube 1·3 cm. bore resulting in the establishment of the detonation wave. (Bone, Fraser, and Wheeler)

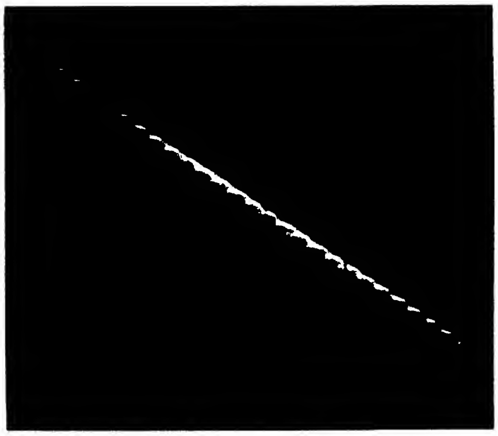


FIG. 18. The spinning detonation wave in a mixture of $2CO + O_2$ in a tube 1·3 cm. diameter. Rotational speed 44 000 per sec. Detonation speed 1,760 m. per sec. (Fraser)

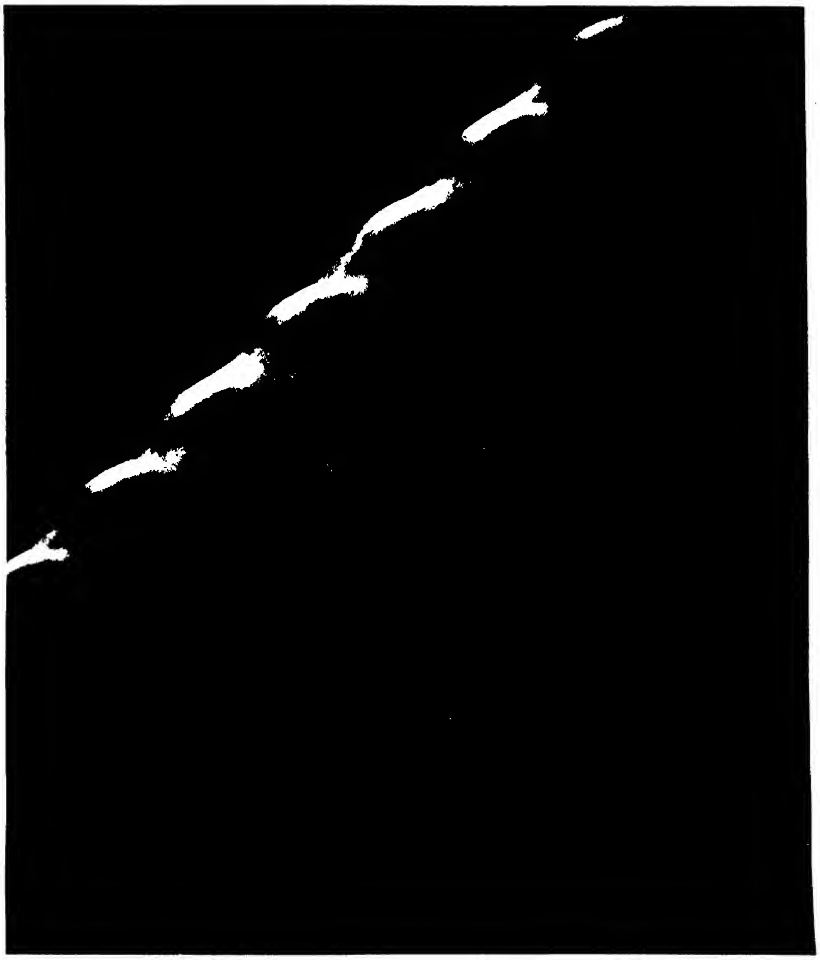


FIG. 19. High-speed analysis of the spinning detonation wave in $2CO + O_2$, showing the horizontal bands in the photograph to be composed of luminous patches produced by the criss-crossing of two sets of luminous diagonal lines. (Time represented by picture = 1/10,000 sec.)

Fig. 20. Instantaneous direct shadow snapshot of the shock wave ahead of the flame at the instant before detonation. (Exposure = 10^{-6} sec.) (Fraser)

it. This is the familiar phenomenon of 'ignition ahead' already described. It gives good ground for the assumptions made above.

If an explosion wave in such a mixture is travelling along a tube, it may be assumed that originally the flame front is a plane perpendicular to the tube axis. By symmetry the radiation in front of the flame is a maximum near the centre of the tube, and in consequence of this the burning will be more rapid near the axis. The flame front will tend, therefore, to become attenuated or cone-shaped. On this assumption the point of the cone is necessarily the seat of the most intense burning in the front and also the seat of the most intense radiation, so that the tendency is for it to become more and more elongated and not to return to its original plane form. Since, however, radiation from the *whole* of the front is effective in exciting the gas ahead even near the point, it is impossible for the cone to burn to an unlimited attenuation, and it will quickly reach a limiting position ahead of the main body of flame, but still supported by the main bulk of radiation. The mixture having still the potentiality for burning at the high rate made possible by the radiation, the rate of burning at the point can be maintained indefinitely at the highest speed at which it will burn, so long as it remains near enough to the body of the flame to receive its supporting radiation. It is quite clear that for the two levels or rates of burning to be maintained together the point must move cross-sectionally in the tube so as to traverse a longer path than that of the main body of the flame. The simplest possible path for it to follow is along a helix. Because of its significance both here and later it should also be noted that on account of the extremely rapid rate of burning there will be a very steep pressure gradient just ahead of the flame, and it is the fact that the flame is burning into this already compressed (as well as excited) gas which maintains this high rate of burning. If through any cause whatever the rate of burning should be slightly diminished, the pressure wave will continue to travel onward at its original speed—although this will gradually decline to the velocity of sound—and the forward velocity of the flame may fall to a comparatively low value through the temporary separation from the pressure it had built up. It will, of course, eventually catch up the lost pressure wave, and redetonate.

The banded and striated appearance of the photographic records is now explicable without the necessity of the assumption that the gases as a whole rotate. It has recently been shown, by taking graphical pictures at very high film speeds by means of The Fraser High-speed Mirror-Camera, that the nearly horizontal light bands, seen in the older pictures, can be resolved into a series of spots of enhanced illumination, arranged horizontally, produced by the criss-crossing of two sets of luminous lines inclined in opposite directions (Fig. 19). From their appearance in the photographs it is clear that the forward set is produced by bunches of burning molecules travelling forward in the explosion tube, while the backward set is produced by pressure waves. Both sets appear to originate in the wave front, and there appear to be two pairs produced during each helical rotation. It is not immediately obvious that this discovery is of much assistance in deciding the source of the bands, for it is difficult at first to see any compatability between the continuous spiral motion as proved by the silver cut-helix, and the discontinuous nature of the recurring pressure waves.

It can be shown geometrically, however, that as the point of the flame cone travels along its helical path, starting from any point in the tube and then considering the position when it has moved through half a pitch, there will be a small pocket of unburnt gas enclosed on three sides by flame. It can be fairly assumed that this pocket of gas would explode spontaneously in these circumstances, giving rise to a pressure wave, and producing a local incandescent mass of gas which would be carried forward by the rush of burning medium behind the front. The process would be repeated indefinitely, but not necessarily at exactly half-rotation intervals, though nearly so.

If any further proof were needed that the mass of gas as a whole is not rotating, it is afforded by the fact that photographs have recently been obtained which show all the characteristics of spin, though the detonations took place in tubes of triangular square and rectangular cross-section. It must be admitted that there is little likelihood of the gas rotating at the same speed in these conditions as it would in a circular tube; and in further support of the view outlined above, which assumes no dependence upon the burning of any particular gas to produce the spinning detonation-wave, it has recently been shown that several gases hitherto regarded as having non-spinning detonation-waves show well-defined spin when mixtures near the detonating limits are exploded. The case of pentane with air or with oxygen can be quoted as a characteristic example.

Furthermore, by means of instantaneous direct shadow-snapshots recently obtained, both the detonation wave and the shock wave before the instant of establishment of detonation have been photographed. These photographs confirm the new view outlined and show no evidence of rotation of the high-pressure gases as a whole. They show clearly the shock wave ahead of the flame at the instant before detonation, and that at this time it exists as a flat disk at right angles to the tube axis (Fig. 20), but that in the spinning detonation wave the flame front is attenuated and the pressure distribution is more complex. Further work, however, is necessary before the true contour of the wave front can be determined with exactitude.

The most recent work shows that spin is of quite general occurrence in gaseous detonation in the tube, and that for all gases mixed with oxygen or air there is a fixed relationship between the helical speed of the rotating part of the wave and the forward speed of the wave, and it is thought that the head of detonation follows a helical path of almost exactly the same pitch for all detonating gas mixtures.

'Detonation' in Engines.

The use of the term detonation in connexion with 'knock' in engines has become widespread. This is perhaps unfortunate, for in the strict scientific sense it is very doubtful whether true detonation could be produced in an engine combustion chamber under working conditions. Many authors have gone even farther and distinguished various so-called varieties of detonation wave, using the terms 'knocking', 'pinking', 'bumping', &c., to describe the various noises associated with these modes of burning.

It seems unnecessary to consider the establishment of a detonation wave (as described in the previous section) as being the explanation of the high rate of burning involved in a knocking explosion. Such high rates are more easily explained by reason of the presence of compression waves. It has previously been shown that all explosions of a vibratory or turbulent nature, whether quiescent initially or not, produce compression waves at some stage during the flame progress, resulting in the later stages of combustion being largely influenced by them. By analogy, therefore, it seems probable that, in the engine where the hot compressed gases *ahead of the flame* are unstable in the sense that pre-oxidation has to some degree occurred and highly inflammable centres have been produced (cf. other articles of this series), such a wave would spontaneously ignite the gases in its path either at its first passage or at some later one, resulting in an extremely rapid combustion akin to detonation. Furthermore, a compression wave in the relatively short combustion chamber of an engine would have an extremely high frequency of reflection from the walls, giving rise to audible vibration of the metallic parts. Pressure diagrams of explosions exhibiting 'knock' show rapid oscillations at the indicator. It is reasonable to suppose that these transient pressures result from the continually reflected pressure waves of high intensity. According to the temperature of the medium a wave may have a velocity as high as 800 to 1,000 metres per sec., so that, for example, in a combustion chamber 3 in. long a frequency of reflection of over 10,000 per sec. would be possible during the later stages of burning. Such a high frequency of repeated wave compression and disturbance of the flame gases could only lead to complete and extremely rapid burning.

Pressure waves will lose their energy mainly by the process of reflection and interference. The process will be relatively slow, so that once formed, the waves are difficult to remove or destroy. It is evident, however, that the form of the combustion chamber will have considerable influence in this respect.

It is now generally accepted that centres of high energy in the unburnt gases may be promoted by both normal compression in the engine and any sudden local rise of temperature and pressure, as may be caused by hot areas of the combustion-chamber wall or through the additional compression of part of the gases ahead of the flame envelope. Inhibitors of the initial combustion occurring at these centres of activation in the unburnt gases will minimize or even prevent the spontaneous ignition by a compression wave.

Although the presence of compression waves in an explosion may be influential in promoting 'knock', it is not necessary to suppose that their presence is an assurance of it, for it is probable from what has been seen in the laboratory that all gaseous explosions are complicated by such waves. They must, however, be taken into account in any explanation of the phenomenon.

REFERENCES

1. Bone, W. A., and Fraser, R. P. *Phil. Trans., A*, **228**, 197 (1929).
2. —— *Phil. Trans., A*, **230**, 371 (1931).
3. Bone, W. A., Fraser, R. P., and Wheeler, W. H. *Phil. Trans.*
4. Bone, W. A., Fraser, R. P., and Winter, D. A. *Proc. Roy. Soc.* **114**, 402 (1927).
5. Campbell, C. *J.C.S.* 1572 (1927).
6. Campbell, C. and Finch, A. *J.C.S.* 2094 (1928).
7. Campbell, C. and King. *Manchester Memoirs*, no. 5, lxxvi (1931–2).
8. Campbell, C., and Woodhead, D. W. *J.C.S.* 3010 (1926).
9. Cranz, C. *Z. ang. Chem.* **36**, 76 (1923).
10. Dixon, H. B. *Phil. Trans., A*, **200**, 315 (1903).
11. —— *J.S.A.E.* **9** 239 (1921).
12. Ellis, O. C. *Fuel in Science and Practice*, **169**, (1928).
13. Fraser, R. P. *J. Roy. Photo. Soc.* **74**, 388 (1934).
14. Fraser, R. P. *J.S.C.I.* **49**, 99 (1930).
15. Hunn, J. V., and Brown, G. G. *Ind. Eng. Chem.* **20**, 10 (1928).
16. Mallard and Le Chatelier. *Annales des Mines*, 8e Sér. **4**, 274 (1883).
17. Mason, W., and Wheeler R. V. *J.C.S.* **115**, 578 (1919) and **117**, 36 (1920).
18. Payman, W., and Shepherd, W. C. F. *Safety in Mines Research Board Paper*, no. 29 (1926).
19. Payman, W., and Wheeler, R. V. *Trans. Chem. Soc.* **120**, 363 (1922).
20. Shtsholkin, K. L. *Phys. Z. der Sowjetunion*, Band 6, Heft 1–2 (1934).
21. Topler. *Ann. der Phys. Chem.* **131**, 33 (1867).
22. White, A. G. *Trans. Chem. Soc.* **121**, 2561 (1922).
23. Woodbury, C. A., Lewis, H. A., and Canly, A. T. *J. Soc. Autom. Eng.* **8**, 209 (1921).

9. FLAMES OF HIGH-SPEED DETONATION

By Professor P. F. LAFFITTE

University of Nancy

THIS article deals with the propagation of flame at velocities greater than 1,000 m. per sec., i.e. by the mechanism of the explosion wave (detonation). It deals particularly with the promotion and propagation of the explosion from the experimental and only slightly from the theoretical point of view. It ends by citing a certain number of cases where propagation of flames have been observed having velocities which, although inferior to those of explosion waves, are nevertheless greater than those of normal combustion (uniform movement of flame). Whenever possible the phenomena studied in the laboratory are compared with those observed in internal-combustion engines. This leads to the consideration of the phenomenon of 'knock'. But this question is not treated in entirety, as it is discussed in other articles. The discussion is limited to the comparison of the velocity of flames in engines with that of the explosion wave; the author's personal opinion, based mostly on his own experiments, is given and the article discusses the possibility of the promotion of a true explosion wave in the combustion with knock of combustible mixtures in engines. Similarly, allusion has only been made to the following subjects, which are discussed elsewhere: to vibratory flames and shock waves, and to waves which give striae on the photographic records (only alluding to the author's own work on this subject). The influence of radiation, ionization, and temperature of explosion have not been discussed, as most of the experiments on these subjects relate rather to combustion than to detonation.

Explosion Wave (Detonation).

In 1881–2 Berthelot and Vieille [3], on the one hand, and Mallard and Le Chatelier [41, 1883], on the other, measured velocities of propagation of combustion which were in fact greater than any velocity of combustion which had previously been observed. While velocities of the order 1 m. per sec. were the highest then known, the experiments of the above authors showed that in certain conditions and for certain combustible mixtures, explosive phenomena can be propagated at velocities of several thousand metres per sec. (the velocity being definitely uniform for a mixture of definite composition).

These results led Berthelot to conceive of a new way in which explosive phenomena could be propagated, i.e. propagation by an explosion wave corresponding to detonation of the gaseous mixture. Two possible methods of decomposition had already been postulated for solid explosives (Roux and Sarrau [49, 1873]). Berthelot thought that the propagation of detonation was not simply by thermal conduction, as in ordinary combustions, but that it took place by the following mechanism (this has been confirmed by many later experiments). A layer of gaseous mixture being rapidly taken to a high pressure, its temperature increases until the ignition-point is reached, when combustion takes place. This results in compressing the next layer which then burns, the effect being that in the explosion wave combustion is transmitted along with the wave of high pressure. Thus there is a juxtaposition of mechanical and chemical phenomena; in other words, the explosion wave is characterized by the union of the shock wave and of the flame. For this reason one can sometimes speak of the explosion wave being at the same time a shock and combustion wave (Jouguet [28, 1907]). It is a chemical reaction (limited at times owing to chemical equilibrium by back reaction) which is propagated in the explosion wave and which communicates to the moving system a considerable excess of velocity, while the sound wave is only transmitted with a very slight excess of pressure and a velocity determined only by the physical constitution of the vibrating medium. The velocity of the explosion wave is also much greater than that of sound waves transmitted in the same medium (Berthelot [2, 1882]; Dixon [15, 1893]). However, the explosive wave is propagated in a given medium with a constant velocity in the same way as the sound wave. In the case of the sound wave a train of waves is propagated, while the explosion phenomenon gives place to a single wave. In the internal-combustion engine the normal régime corresponds to a simple combustion, and it is only in quite exceptional cases that favourable conditions for the development of a true detonation would present themselves. These conditions would be realized according to certain theories when 'knock' is set up. This point will be referred to later. During the last 12 years a great number of investigations have been made in order to study this question. A résumé of the principal results of these will be given, at the same time referring to investigations which have had a purely scientific aim. But first a few brief references will be made to theories of the explosion wave.

Theories of the Velocity of Detonation.

Berthelot [2, 1882] related the velocity of propagation of detonation to the mean kinetic velocity of the molecules in gases raised to a high temperature by the combustion which takes place at the front of the wave. But velocities so calculated differ often to a rather large extent from the velocities determined experimentally.

Dixon [15, 1903] obtained better results by comparing the velocity of the explosion wave and the velocity of sound in the same gaseous mixture.

But the true theory of the explosion wave is due to Chapman [13, 1899] and to Jouguet [28, 1905]. Both of them started from the work of Hugoniot [26, 1887] on the propagation of shock waves in inert fluids, when no chemical reaction takes place.

According to the theory of Hugoniot, any movement in a gas which is at rest propagates itself with a velocity equal to the normal velocity of sound so long as no discontinuity is produced (as, for example, by a sudden rise in pressure). But if there is a discontinuity (as happens when a shock wave is propagated or when a layer of the gaseous mixture passes from the initial pressure to a pressure which may be very high), each of the layers which are affected undergo a sudden change of pressure and consequently of density. If the discontinuity is produced in a way which compresses the gases, the velocity of propagation is faster than the velocity of sound. In order to explain the detonation, Chapman, and also Jouguet, postulated that the transmission of the pressure entailed a chemical change in the medium. Jouguet also allowed that the chemical reaction took place on the front of the explosion wave, and that the gases in question were perfect gases, but he postulated that the specific heat was a function of the temperature. He also took into account certain experimental conditions (uniform velocity, &c.). The velocities so calculated are often very near those determined experimentally, and from that point of view this theory is quite satisfactory.

Many different theories have been put forward recently (Semenoff [50, 1928]; Garner [24, 1930]; Lewis [39, 1930]; Muraour [44, 1932]; Andreef [1, 1933]), all based on the transmission of reaction by chains. Only the theory of Lewis enables the velocity of detonation to be determined. This author starts with the principle of the equi-distribution of energy between the different degrees of freedom of the products of the elementary reaction. He calculates the velocity of propagation of these products from the quantity of energy corresponding to their degree of kinetic freedom, and in some cases the results obtained are in excellent agreement with the experimental results.

These theories have sometimes been objected to on the ground that they should be equally applicable to combustion as to detonation, but would give too great velocities for ordinary propagation. Perhaps this criticism is better justified for the molecular than for the hydrodynamic theories, as the latter are based on the rapid rise of pressure in front of the explosion wave, and the theory of Jouguet in particular allows one to differentiate combustion from detonation [29, 1913].

Experimental Methods for studying Detonation.

Measurements of velocities of detonation can be made with precision by chronographic methods (Berthelot [3, 1882]; Dixon [15, 1893]), or by photographic methods. This latter method, first employed by Mallard and Le Chatelier [41, 1883], is now generally used. It not only determines the velocity of the wave, but is of use in the study of all the phenomena which accompany the formation or the propagation of detonation. It has rendered, and is still rendering, valuable information on these points. It consists in photographing the propagation of the luminous phenomenon on a film moving with a known velocity (rolled, for example, on a revolving drum). The only objection which might be made against the method of Mallard and Le Chatelier is that it only allows of the recording of flames of sufficient actinic power to influence the sensitive film. But for flames with poor or no luminosity photographic methods have been devised recently (White [53, 1928]; Payman [46, 1926]; Laffitte and Patry [36, 1930]) which have not yet rendered all the service which may be legitimately expected from them. They are adapted from the Schlieren or the shadow methods, and are based on phenomena of refraction of light; a photograph of the front of a non-homogeneous flame or of a shock wave is obtained by means of the deviation of a part of the rays of light coming from an auxiliary luminous source; on the photograph a line (dark on the positives and light on the negatives) is obtained by interference with the image of the luminous bundle of rays from the auxiliary source (cf. Article 8 in this Section).

Setting up of Detonation—Detonating Mixtures.

All combustible gaseous mixtures do not detonate, i.e. give place to the propagation of an explosion wave. This is particularly so in the case of mixtures of air with illuminating gas or with a large number of hydrocarbons. With oxygen, on the contrary, most of the hydrocarbons give an explosion wave, even for concentrations of gaseous mixtures some way from the theoretical concentration (Dixon [15, 1903]). If nitrogen is added to the mixture, it usually loses its detonating quality before the proportion of nitrogen is reached corresponding to the composition of air. It may be noted that a mixture may not be susceptible to detonation at atmospheric pressure, but may give an explosion wave at a suitable pressure. There is as yet no direct experimental confirmation of this fact, but it is a consequence of the results of researches on the influence of pressure on the formation of an explosion wave. Finally there are no experiments recorded on detonation in mixtures to those used in internal-combustion engines for precisely similar pressure and temperature conditions (cf. Article 1).

Detonation Limits.

An explosion wave is only formed between certain well-defined limits in a suitable mixture, and these are called *limits of detonation.* Wendlandt [52, 1925] determined the lower limits of detonation in hydrogen-air and carbon monoxide-oxygen mixtures. Laffitte and Breton [33, 1934] have recently undertaken the systematic study of the detonating region in a certain number of gaseous mixtures. But as in the neighbourhood of the limits the detonation phenomenon does not provide sufficient light to be photographed, they were obliged to employ the method using auxiliary lighting in which the front of the explosion wave is registered by a very fine mark on the photograph, by the interruption of the light from the luminous source (Figs. 1 and 2). The following are the results obtained with mixtures at 1 atm. pressure (tubes 14 mm. internal diam.).

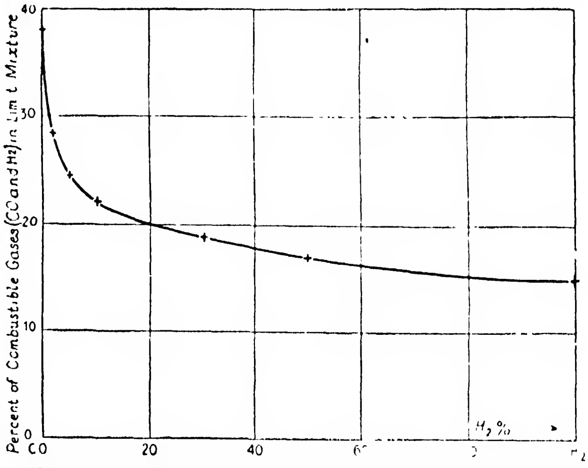


FIG. 3. Lower limit of detonation for the mixtures of carbon monoxide-hydrogen-oxygen.

Mixtures	*Lower limit*	*Upper limit*
	(% of combustible gas in air or oxygen)	
H_2—O_2	15	90
H_2—air	18·3	58·9
CO—O_2	38	. .
$(CO+H_2)$—O_2	17·2	91
$(CO+H_2)$—air	19	58·7
(C_3H_8)—O_2	3·2	37
Iso-C_4H_{10}—O_2	2·8	31·1
NH_3—O_2	25·4	75·4
C_2H_2—air	4·0	51

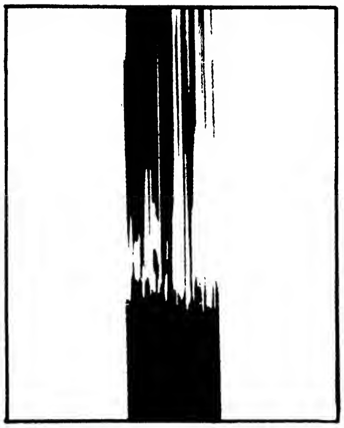


FIG. 1. Detonation wave in propane $C_3H_8 + O_2$ (36.5% C_3H_8)

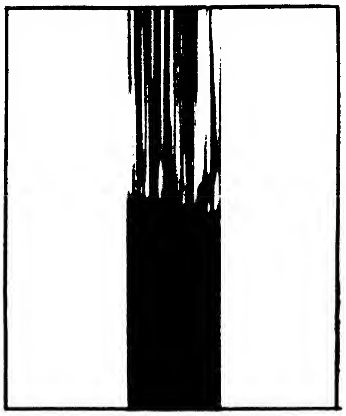


FIG. 2. Detonation wave in propane + O_2 (36.8% C_3H_8)

In these two photographs the front of the explosion wave, as shown by the inclined white line, has interrupted the light from the auxiliary source represented by the black band. The trajectories of the waves are seen to be helicoidal. The streaked aspect of the upper part of the photographs is due to the breakage of the glass tubes

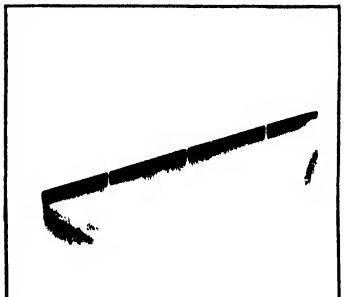


FIG. 5. Detonation wave in $CS_2 + 3O_2$

Fig. 4. Formation of detonation wave in the mixture $CS_2 + 2.5O_2$

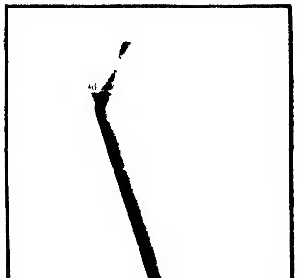


FIG. 6. Formation of explosion wave in the mixture $2H_2 + O_2$ at 6 atm.

The presence of small quantities of a foreign gas can modify to a great extent the detonation limits of gaseous mixtures (Laffitte and Breton [33, 1934]). Thus the replacement of 2% of carbon monoxide by an equal quantity of hydrogen lowers the lower limit of detonation in mixtures of CO and oxygen from 38 to 28·4%. After this, further amounts of hydrogen produce less and less important effects (Fig. 3).

Mechanism of the Formation of an Explosion Wave.

It is interesting, both from the theoretical and practical points of view, to see how the explosion wave is set up in the detonating mixture. Actually detonation is not set up instantaneously after the action of the igniting agent (usually an electric spark). Thus in a cylindrical tube a flame is first propagated of which the velocity increases. In certain cases this flame may be subject to vibrations of larger or smaller amplitude (Mallard and Le Chatelier [41, 1883]). Then at a given moment the explosion wave is suddenly set up, usually without there being continuity between the velocity of the propagation of the flame and that of the explosion wave (Fig. 4). From this moment the flame is propagated at a strictly uniform velocity (Fig. 5). The explosion wave being formed by the juxtaposition of a flame and a compression wave, the detonation is set up at the moment when the flame front and the front of the compression wave coincide. At the moment when the mixture is ignited the expansion of the burnt gases in the first gaseous layer compresses the second layer before the latter is ignited. Moreover, in many cases the electric igniting spark gives rise to the formation and propagation of a compression wave, but it is much weaker than that which is formed at the time of ignition. Thus a compression wave precedes the flame. The velocity of the flame is increasing, as is shown on all the photographs. A moment arrives when it overtakes the compression wave, and this is the instant when the explosion wave is set up. Payman [45, 1928], however, while photographing the shock wave at the same time as the flame, observed that the compression wave which set up the explosion wave originated in the gases which had already been traversed by the flame and in which combustion had already started. In other experiments, however, it has been observed that detonation could be set up at a point before the arrival of the flame: for example, Campbell and Woodhead [12, 1926] by placing an obstacle in the tube, and Laffitte and Dumanois [34, 1926] by increasing the pressure (Fig. 6). Jouguet [28, 1907] and Crussard [29, 1914] explain this phenomenon in the following way: During the variable predetonation period the compression wave becomes modified as it goes forward. If the discontinuity that it is propagating is accentuated, a moment arrives when the temperature reached at the front of the wave is such that ignition occurs without delay. At this moment there are propagated (1) towards the front a shock and combustion wave which is in fact the explosion wave, and (2) in the backward direction, a retrograde wave which sets up combustion in the part of the mixture between the compression wave and the flame, and which, after its encounter with the flame, continues to be propagated in the half-burnt gases as a compression and combustion wave. This phenomenon has also been obtained by Laffitte [31, 1925] when the interior walls of the cylindrical tube in which the explosion is propagated present irregularities; as these irregularities favour an increase of pressure in the front of the compression wave, they cause a kind of auto-ignition of the mixture leading to detonation at a point which the flame has not yet reached. As a result the detonation is much more quickly set up in a tube with rough than in a tube with perfectly smooth walls (all other conditions being the same).

Influence of various Agents on the Setting up of Detonation.

The setting up of the explosion wave naturally depends on the igniting system (flame, hot walls, adiabatic pressure, electric spark, &c.), and in the case of an electric spark its powerfulness has a great influence on the setting up of the detonation. Thus the detonation is not definitely set up unless the spark is sufficiently powerful, otherwise the variable period which precedes it may be prolonged for some little time (Berthelot [3, 1883]; Dixon [15, 1903]).

For a given mixture the concentration of combustible gas has a great influence on the length which the flame traverses before setting up the explosion wave (Le Chatelier [37, 1900]). In many cases it is not in a mixture of stoichiometric composition that detonation is most rapidly set up. Often it is in a mixture richer in combustible gas than the theoretical mixture that the length of the combustion preceding the setting up of detonation is at a minimum. This is exactly what occurs in an internal-combustion engine, where the proportion of combustible gas/air is higher than the theoretical proportion for complete combustion. This remains to be verified experimentally. One must, however, note in connexion with this that the presence of *steam* in the combustible mixture favours the setting up of detonation in certain cases (mixtures based on CO).

Another factor which influences the formation of the explosion wave is the *diameter* of the tube. Thus the detonation is more easily set up when the diameter of the tube is smaller. The following table gives the distances from the igniting spark at which the explosion wave is set up in a mixture of carbon-disulphide and oxygen (CS_2+3O_2) (Laffitte [31, 1925]).

Diameter (*mm.*)	*Distance* (*cm.*)
6·5–7	48
16	52
24	58
34	84
43	105
54	131

It may be noted that even with a tube of relatively small diameter (in comparison to those dimensions used in practice) the flame is propagated for a considerable distance before the explosion wave is formed, and this is the case even for a mixture which detonates easily (mixture based on oxygen and not on air). At constant diameters the setting up of detonation is delayed by the increase of the initial temperature of the combustible mixture (Laffitte [32, 1928]). The following table gives the distances traversed by the flame before the setting up of detonation for a hydrogen and oxygen mixture and for a methane and oxygen mixture:

$2H_2+O_2$ *mixtures*		CH_4+2O_2 *mixtures*	
Initial temperature (0° *C.*)	*Distance* (*cm.*)	*Initial temperature* (0° *C.*)	*Distance* (*cm.*)
15	60	15	55
120–30	73	160–80	74
160–80	78	290–310	90
300-20 340–60	(no detonation; tube 100 cm. long)	340–60	(no detonation; tube 100 cm. long)

Thus the nearer the temperature of spontaneous ignition of the mixture is approached the more difficult it becomes for the explosion wave to be formed. On the contrary, the more the *initial pressure* of the mixture is raised, the sooner detonation is set up, as is shown by the following table:

$2H_2+O_2$ *mixture*
(Laffitte and Dumanois [34, 1926])
Glass tube, 25 cm. diameter

Initial pressure (atm.)	*Distance (cm.)*
1	70
2	60
3	52
4	44
5	35
6	30
6·5	27

$C_2H_2+2{\cdot}5O_2+4N_2$
(Egerton and Gates [23, 1927])
Steel tube, 15·87 mm. diameter

Initial pressure (atm.)	*Distance (cm.)*
1	52
2	30
3·7	22
4·1	18

$C_5H_{12}+8O_2+6N_2$ *mixture*

1	70
2·7	37
4·4	32
5·1	31

$C_5H_{12}+8O_2+15N_2$ *mixture*

2	100
5·4	72
9·3	74

The presence of an anti-knock in the gaseous mixture under pressure has not much influence on the setting up of detonation at either normal temperature or at higher temperatures, as has been shown by the experiments of Egerton and Gates [23, 1927] on mixtures of pentane, oxygen, and nitrogen; experiments were made at higher pressures also, but only in the case of slow vibratory flames was any delaying effect observed.

The Explosion Wave in Internal-combustion Engines.

From the above results it does not seem probable that a true detonation can be set up in an internal-combustion engine, chiefly on account of the small length of the cylinder. Furthermore, the mixtures used, being diluted by the large amount of nitrogen in the air, are much less explosive than the mixtures used in the above experiments which were either made with pure oxygen or with oxygen diluted with a relatively small amount of nitrogen and with combustible gases which detonate easier than those used in internal-combustion engines. However, it is important to notice that though the conditions for a true explosion wave do not seem to be normally realized in an internal-combustion engine, it is very possible that combustion can be propagated in it at relatively high velocity although less than those of a true explosion wave (flame of accelerating speed preceding the setting up of the explosion wave). Further, it has been observed by the author that when the cylindrical tube in which the explosion is propagated is not long enough for detonation to be set up in it, at the moment that the front of the flame arrives at the end of the cylinder a retrograde reflection wave is produced which returns into the incompletely burnt gases, completing their combustion. The velocity of this retrograde wave is sometimes very high (of the order of many hundreds of metres per second), and in consequence could be, in certain cases, the cause of the phenomenon of knock without its being necessary to postulate the formation of a true explosion wave. The phenomena registered photographically in internal-combustion engines will be referred to later. However, the possibility of the existence of detonation under the special conditions which determine the functioning of internal-combustion engines must not be entirely rejected. Thus it has been postulated (Moureu, Dufraisse, and Chaux [43, 1927]; Dumanois [20, 1928]) that the violent decomposition of the unstable and explosive peroxides, formed transitionally in the reactions of pre-combustion of the vapours of the combustible liquids, might set up the detonation (the presence of these in engines under knocking conditions has been observed directly by Dumanois, Mondain-Monval, and Quanquin [22, 1931]). This suggestion has not been verified experimentally, but is based on the fact that the presence of an initiating explosive, such as fulminate of mercury, instantly sets up an explosion wave (Laffitte [31, 1925]). This has also been confirmed by Bone and Fraser [5, 1931], who showed that detonation could be set up at the moment of ignition, provided that the latter was sufficiently intense, and that the flame was at the same time submitted to a sufficiently powerful shock wave.

In support of the above hypothesis, according to which the decomposition of peroxides would be able to set up detonation, one could cite the fact that the explosion wave of a first mixture generally sets up detonation in a second mixture after a very short distance if the velocity of detonation of the second mixture is less than that of the first (Campbell and Woodhead [12, 1926]). But it would still have to be verified that the decomposition of peroxides can be caused by an explosion wave and also that the decomposition is propagated at a velocity greater than that of the initial mixture.

If the above hypotheses should be confirmed, the explosion wave could be set up simultaneously in many points in the combustible mixture; this would, moreover, increase the violence of the knock, and the more because every time an explosion wave is set up there is a simultaneous formation of a shock wave which is propagated in the gases in the opposite direction to the explosion wave (Le Chatelier [37, 1900]). (These waves are shown on all photographs (Figs. 4 and 6).) These different shock waves may interfere with each other or with the reflection waves formed when they reach the walls of the cylinder, and may also produce, at the points of interference, much higher pressures which would have severe mechanical effect. Certain experiments (Laffitte [31, 1924]) have also shown, both in the cases of a simple combustion and of a detonation, that the glass container only shatters after multiple reflections on the walls either of the flame or of compression waves.

The Propagation of Detonation. Velocity of the Explosion Wave.

Once it has been set up, the detonation is propagated at a strictly uniform velocity in a stable mixture (Berthelot [2, 1882]; Mallard and Le Chatelier [41, 1883]; Dixon [15, 1893]) (Fig. 5). This velocity does not depend on the material of which the tube is made containing the explosive mixture: the velocity of propagation of an explosion wave

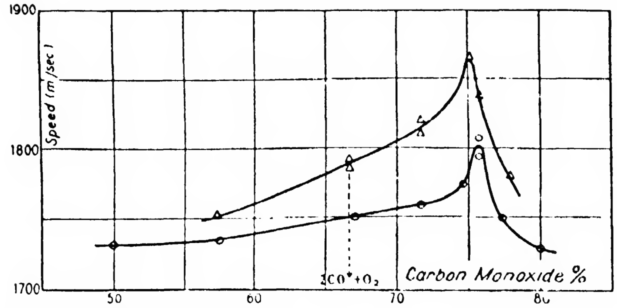


FIG. 7. Velocities of detonation of wet mixtures of carbon monoxide and oxygen

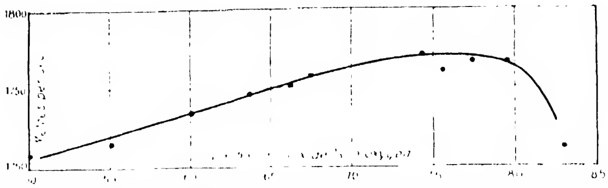


FIG. 8. Velocities of detonation of dry mixtures of carbon monoxide and oxygen

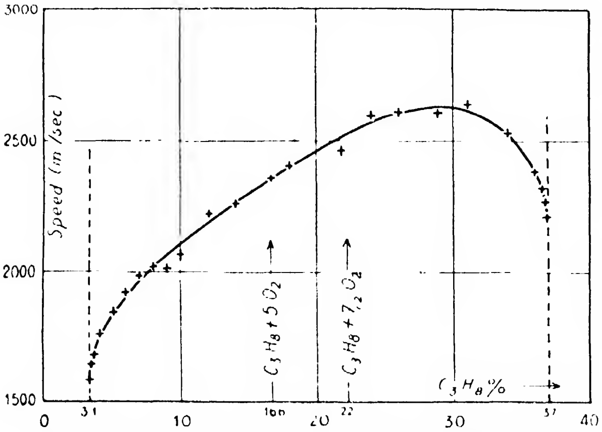


FIG. 9. Limits and velocities of detonation of mixtures of propane and oxygen

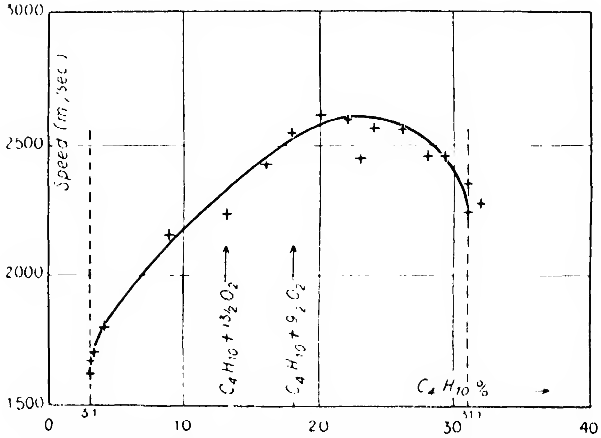


FIG. 10. Limits and velocities of detonation of mixtures of butane and oxygen

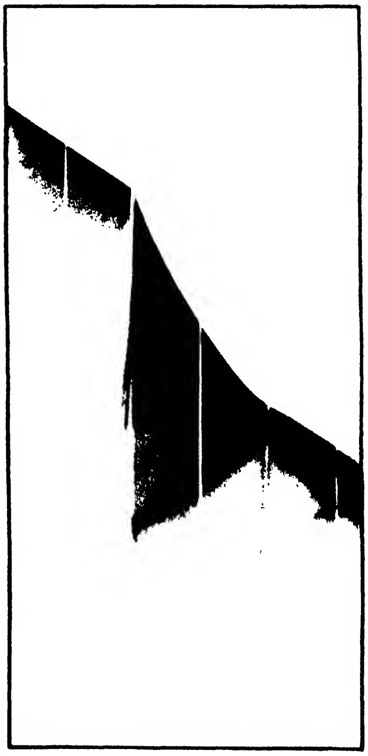


FIG. 12. Passage of the detonation wave from a tube 7 mm. diameter to a tube 33 mm. diameter for the mixture CS_2+3O_2

is the same whether the tube is made of steel, lead, tin, glass, or rubber (Berthelot and Vieille [3, 1882]). However, Campbell, King, and Whitworth [8, 1932] have shown that in the case of tubes of rubber this only holds for normal detonation ($2H_2+O_2+N_2$, CH_4+2O_2, $2CO+O_2+7\%$ H_2, &c.). In the case of explosion waves which give striation on the photographic records ($2CO+O_2$, $2H_2+O_2+CO_2$, CH_4+7O_2) an appreciable diminution of velocity has been observed with rubber tubes; this diminution depends on the length and thickness of the rubber tube.

Every velocity of detonation which has been measured at present has always been found to be between 1,000 and 4,000 m. per sec. A certain number of values are collected in the following table:

Mixture	*Velocity (m. per sec.)*	*Author*
$2H_2+O_2$	2,821	Dixon
$2CO+O_2$	1,089	"
CS_2+3O_2	1,800	Le Chatelier
CH_4+2O_2	2,146	Dixon
$CH_4+1{\cdot}5O_2+2{\cdot}5N_2$	1,880	"
$C_2H_6+3{\cdot}5O_2$	2,363	Berthelot
$C_2H_4+3O_2$	2,209	Dixon
$C_2H_4+2O_2+8N_2$	1,734	"
$C_2H_2+1{\cdot}5O_2$	2,716	"
$C_2H_2+1{\cdot}5O_2+N_2$	2,414	"
$C_2H_6+3O_2$	2,600	Laffitte and Breton
$C_3H_8+6O_2$	2,280	" "
$C_4H_{10}+4O_2$	2,613	" "
$C_4H_{10}+8O_2$	2,270	" "
$C_5H_{12}+8O_2$	2,371	Dixon
$C_5H_{12}+8O_2+24N_2$	1,680	"
$C_6H_6+7{\cdot}5O_2$	2,206	"
$C_6H_6+22{\cdot}5O_2$	1,658	"
$C_2H_5OH+3O_2$	2,356	"
$C_2H_5OH+3O_2+12N_2$	1,690	"

The velocity of propagation of the explosion wave is usually independent of the diameter of the tube, provided that the diameter is not less than several millimetres (Berthelot and Vieille [3, 1882]).

As an exception, however, Bone and Fraser [5, 1931], as well as Campbell [6, 1922], have observed differences in velocity which may reach 100 m. per sec. using mixtures of carbon monoxide and oxygen saturated with water at 18° C. when the diameter of the tube was changed from 15 to 25 mm. The following table gives the velocities of the wave in various concentrations of carbon monoxide for both diameters (Fig. 7):

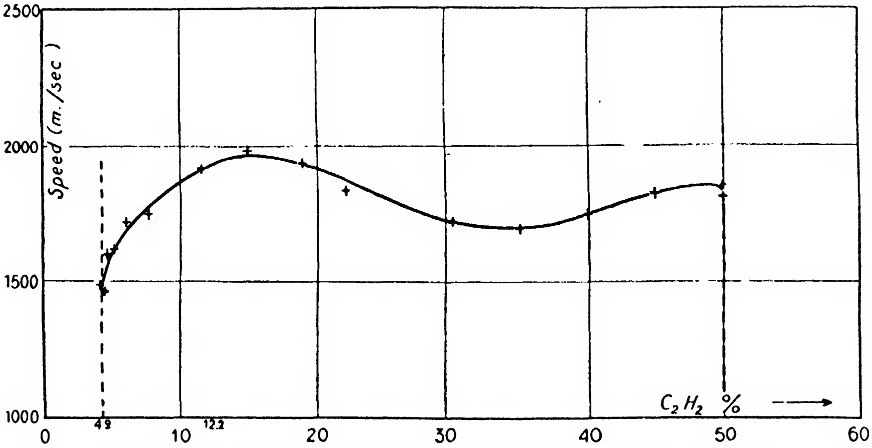


FIG. 11. Detonation limits and velocities of mixtures of acetylene and oxygen.

I. Tube 13 mm.		*II. Tube 25 mm.*	
% CO	*Velocity (m. per sec.)*	% CO	*Velocity (m. per sec.)*
50·0	1,732	57·0	1,752
57·6	1,735	66·6	1,795
67·0	1,750	71·6	1,825
71·8	1,760	75·0	1,870
75·6	1,809	75·4	1,780
77·6	1,750	77·8	. .
80·0	1,730		

The velocity of propagation of detonation remains the same if the mixture is subjected to a magnetic field (Dixon, Campbell, and Slater [17, 1914]) or to the action of a transverse electric field (Malinowski, Naugolnikow, and Tkachenko [40, 1934]).

In the neighbourhood of the limits of detonation the velocity of propagation of the explosion wave decreases very rapidly. As a result the velocity passes through a maximum for a mixture of a given composition; cf. the following examples: carbon monoxide-oxygen (Campbell, Whitworth, and Woodhead [10, 1933]) (Fig. 8), propane-oxygen (Fig. 9), and butane-oxygen (Laffitte and Breton [33, 1934]) (Fig. 10) (unpublished works). The maximum velocity only rarely corresponds with the theoretical mixture for complete combustion (Figs. 7, 8, 9, and 10).

In general, the concentration of combustible gas corresponding to the maximum velocity mixture is higher than that of the stoichiometric mixture and is near the upper limit of detonation. However, in certain cases the curves of the velocities of detonation as a function of the concentration are not the same shape as those of the above examples (Laffitte and Breton [33, 1934]). Thus with mixtures of ammonia and oxygen the velocity of the explosion wave increases rapidly in the neighbourhood of the two limits of detonation before suddenly decreasing. In mixtures of acetylene and oxygen the shape of the curve is again different (Fig. 11). For 4·2% (lower limit) to 20% of acetylene in air the curve is normal, with a maximum in the neighbourhood of 15%, i.e. a little above the concentration (12·2% of C_2H_2) which corresponds to the total combustion into carbon monoxide and water. An upper limit at a concentration of about 23–25% of acetylene was expected; but from a little above 30% the velocity increased and continued to do so to about 50% of acetylene, which corresponds to the upper limit of detonation. It appears that the second part of the velocity curve should depend on a quite different reaction from that governing the first part (below 23%).

Influence of various Factors on the Velocity of the Explosion Wave.

The presence of very small quantities of *inert gases* or of impurities do not usually modify to an appreciable extent the velocity of propagation of an explosion wave. Water vapour is, however, an exception to this, at any rate in carbon monoxide and oxygen mixtures (Dixon [15, 1903]), and perhaps also in the neighbourhood of the limits of detonation for acetylene-air mixtures (Laffitte and Breton [33, 1934]) (unpublished works). Dixon's results on the influence of water vapour on the velocity of detonation for the mixture $2CO+O_2$ are given in the following table:

Condition	% of steam	Mean rate (m. per sec.)
Well dried	..	1,264
Dried	..	1,305
Saturated at 10%	1·2	1,676
" 20%	2·3	1,703
" 28%	3·7	1,713
" 35%	5·6	1,738
" 45%	9·5	1,693
" 55%	15·6	1,666
" 65%	24·9	1,526
" 75%	38·4	1,266

The velocity thus passes through a maximum for the mixture with 5·6% steam.

The presence of small quantities of anti-knocks, particularly in the case of lead tetraethyl, do not modify the velocity of propagation of the explosion wave in strongly detonating mixtures, as shown by the experiments of Laffitte and Dumanois [35, 1928] on mixtures far from the limits of detonation. The measurements were made on various mixtures of hydrogen or of methane with oxygen which contained about a thousandth part of lead tetraethyl, under initial pressures varying from 1 to 7 atm.

The initial pressure and temperature of the combustible mixture have only a slight influence on the velocity of propagation of detonation, as is shown by Berthelot and Vieille [4, 1882]. The more accurate measurements of Dixon [15, 1903] for a theoretical oxy-hydrogen mixture have, however, shown that pressure has an appreciable influence. But this increase of velocity rapidly diminishes and appears to become insignificant at a pressure higher than 2 or 3 atm.

$2H_2+O_2$

Pressure (mm.)	Velocity (m. per sec.)
200	2,627
300	2,705
500	2,775
760	2,821
1,100	2,856
1,500	2,872

Dixon also proved that pressure exerts the same effect with mixtures of methane and oxygen. But in this case the result has not been confirmed by Sokolik and Shtsholkin [51, 1933], whose measurements appear to be less accurate. Determinations of velocity of detonation have only been made for mixtures under pressure of the vapours of pentane and of acetylene along with various quantities of oxygen and nitrogen (Egerton and Gates [23, 1927]). An observation can be made here on the subject of the influence of the initial temperature. Dixon [15, 1903] has made some accurate determinations (dealing particularly with $2H_2+O_2$, $C_2H_4+2O_2$, and $C_2H_2+O_2$ mixtures) up to temperatures of 100° C. He has shown that an increase of temperature of 100° C. slightly lowers (less than 100 m. per sec.) the velocity of propagation of detonation. This is shown in the following table:

Temperature (° C.)	Velocity (m. per sec.)	
	$2H_2+O_2$	$C_2H_4+2O_2$
10	2,821	2,581
100	2,790	2,538

Laffitte [31, 1925] confirmed and extended Dixon's results (for $2H_2+O_2$ and CH_4+2O_2 mixtures) nearly up to the ignition temperature (450° for the first mixture, 550° for the second). Measurements for mixtures of the vapours of certain hydrocarbons have been made by Egerton and Gates [23, 1927].

It has already been noted that when detonation is set up in a mixture of a given composition, the velocity of propagation of detonation remains constant (for a given temperature and pressure) whatever may be the diameter of the cylindrical tube in which the phenomenon is propagated. But if the tube suddenly increases in diameter, a perturbation is set up at the point of increase, as Campbell [6, 1922] showed for the first time. If the variation in diameter is large enough, there is a sudden loss of pressure on the front of the wave such that the pressure becomes insufficient to propagate the detonation, and a flame of much lower velocity follows it. Thus for $2H_2+3O_2$ mixture detonating at a velocity of 2,120 m. per sec. in a tube of 10 mm. diameter jointed to a tube 30 cm. long with a larger diameter the following velocities were observed:

Diameter of the 2nd tube (mm.)	Velocities (m. per sec.)
23	890
35	640
62	430
85	450
91	440

If the wider tube is sufficiently long the detonation is formed again after a certain distance (Laffitte [31, 1923]) (Fig. 12). The following are the distances travelled by the flame in the second tube before the explosion wave which had been propagated at 1,800 m. per sec. (CS_2+3O_2 mixture) in the first tube of 7 mm. diameter was reformed:

Diameter of the 2nd tube (mm.)	Distance, 2nd tube (cm.)	Mean velocities of the flame in the 2nd tube (m. per sec.)
13	8	1,250 } to the setting up of detonation
16	9	1,200
24	15	1,000
33	50	780 for the first 30 cm.
44	100	235 for the first 50 cm.

This phenomenon is general and can be reproduced in any combustible mixture. Moreover, the above results suggested to Dumanois [21, 1926] the idea of a stepped piston, which he invented in order to suppress knock in internal-combustion engines. A series of steps producing a large increase in diameter in the direction of the propagation of the ignition are fixed on the piston, starting from the ignition-point and arranged in such a way that when the flame reaches a step there is a sudden diminution of velocity of propagation of the explosion. In the case of a detonation the latter changes into a combustion with a slower velocity of propagation, as shown in the above experiments; and even in the case of no actual detonation the velocity of the flame is considerably diminished.

Detonation Pressures.

It is interesting to know the pressure attained in the front of the explosion wave, but the experimental measurement of the value of this pressure is not easy, not only because of the high velocity of propagation of the phenomenon, but also because of the very short time during which this pressure occurs. The importance of the mechanical effects produced by the passage of the explosion wave shows at once that this pressure is much higher than that at the front of a flame even of relatively high velocity. Thus, if a detonating mixture contained in a glass tube of about 10 mm. interior diameter and with walls of about 2 mm. diameter is ignited by an electric spark, it is often found after the explosion that the tube is shattered from the point where the explosion wave was set up, while the anterior part of the tube is still intact.

Dixon and Cain [16, 1894], following a suggestion of Mallard and Le Chatelier, used a method by which glass tubes of known resistance are shattered by the explosion wave. But the results obtained are not very accurate and the value of the method is doubtful (Jones and Bower [27, 1897]).

In some recent experiments, Campbell, Littler, and Whitworth [9, 1932] determined the pressure at the front of the wave by piercing sheets of copper of different thicknesses by means of the explosion wave in various gaseous mixtures.

The copper was calibrated statically using air pressure. The following table gives some of the results thus obtained. The values calculated by Jouguet and by Campbell, Littler, and Whitworth are also given:

Mixtures	*Pressures (atm.). Experimental values*	*Pressures (atm.). Values calculated by:*	
		Jouguet	*Campbell*
$2H_2+O_2$	20·4	17·5	..
CH_4+O_2	34·0	..	36·3
CH_4+4O_2	26·0	..	25·9
$C_2H_4+2O_2$	41·5	..	41·0
$C_3H_4+3O_2$	34·0	..	31·6
$C_2H_2+O_2$	41·5	54·5	..
$C_2H_2+2\cdot5O_2$	34·0	..	30·0
$C_2H_3+7\cdot5O_2$	26·0	..	25·8

In general, the agreement between the observed and the calculated pressures is fairly good except for $C_2H_2+O_2$. In this case the difference seems to be that in the calculation it was assumed that all the carbon was burnt to carbon monoxide, whereas a certain amount of free carbon is always produced in this explosion. Finally, experiments show that the pressure at the point where the explosion wave is set up is higher than in the fully formed explosion wave.

Spherical Explosion Waves—Detonation Spin.

Under all the conditions discussed in the previous pages it has been supposed that the detonation is propagated by a plane wave, that is to say, that the front of the explosion wave is perpendicular to the axis of the tube in which it is propagated. But this is not always so.

Laffitte [31, 1924] has shown that in a spherical vessel, or in a cylinder of large diameter, the detonation may be propagated by a spherical wave. The propagation of such a wave has been recorded photographically; the wave was started by means of a mercury fulminate detonator placed in the centre of a glass globe of several litres capacity which contained a mixture easy to detonate (CS_2+3O_2, $2H_2+O_2$). This phenomenon cannot be observed if the explosion is set up by propagating an explosion wave in a cylindrical tube introduced into the centre of the globe. In this case the wave is destroyed when it reaches the globe and a combustion is propagated with a much lower velocity than that of the wave; this agrees with the remarks already made in connexion with the effect of a sudden increase of tube diameter.

Regarding 'spin', Campbell and his colleagues Woodhead [11, 1927] and Finch [7, 1928], as well as Bone and Fraser [5, 1931], have obtained striated photographic records of the detonation of certain gaseous mixtures. These striae are caused by the detonation being propagated in the tube by plane waves which follow a spiral path. The above authors have provided definite experimental proof of this.

In the preceding article this phenomenon is discussed in greater detail. Laffitte and Breton [33, 1934] have also observed this effect in the case of mixtures of ammonia and oxygen, and of acetylene and air, for the whole length of their detonation. This has also been noted by them for all the mixtures which have been tested (propane-oxygen, butane-oxygen, &c.) in the neighbourhood of the limits of detonation where the phenomenon is not susceptible to photography without recourse to special methods utilizing a supplementary source of light.

Other Flames which are propagated at High Velocity.

There are other methods of propagation of combustion of which the speed is higher than that of the uniform movement of a flame besides that of detonation which is propagated in the explosive mixture at a high and constant velocity by the mechanism of the explosion wave.

But it appears that these other flames nearly always occur with unstable systems (variable velocities): the only two stable systems under definite conditions are the above, i.e. the deflagration, with a low velocity of propagation, and the detonation with a high velocity. Some of the conditions in which such flames of moderate velocity have been observed are as mentioned in the following paragraphs.

1. If the condition of concentration, temperature, and pressure in a cylindrical tube are such that theoretically an explosion wave can be propagated in it, the explosion cannot be set up if the length of the combustion chamber is insufficient. In this case it is observed that a flame is propagated at a constantly accelerating velocity until it reaches the end of the combustion chamber. The velocity of this flame may attain several hundreds of metres and even approach, without, however, reaching, the velocity of the explosion wave. There is usually, in fact, at the moment of the setting up of the detonation a very marked discontinuity between the velocity of propagation of the flame and that of the explosion wave.

2. There are, however, other circumstances besides those of the variable condition preceding the setting up of the detonation, in which flames of great velocity of propagation have been recorded. Thus Mason and Wheeler [42, 1920] have observed that the combustion of methane-air mixtures, under the following conditions, seemed just about to take on the characteristics of a detonation. The flame was propagated in a tube 90 m. long and 30 cm. in diameter open at the two ends and constricted at two points by thin steel rings which reduced its diameter to 28·6 cm.

Chapman and Wheeler [14, 1926] have in a similar way obtained large increases in velocity of propagation of the flame by placing a certain number of constricting rings into the tube in which the combustion was propagated and which was open at both ends. Thus with a mixture of 10% methane in air, burning in a brass tube 240 cm. in length and 5 cm. in diameter, the normal velocity of propagation of flame is 0·70 m. per sec. But if 12 brass rings of 1 cm. thickness and 2·5 cm. interior diameter are placed 5 cm. apart in the tube (the first ring being placed at a distance between 50 and 100 cm. from the end of the tube at which mixture is ignited), the flame is propagated through the constricted region at a velocity of 420 m. per sec. Similar observations have been made by Robinson and Wheeler [48, 1933].

In this case the mechanism of the propagation of flame is not the same as that of an ordinary combustion when the explosion phenomenon is propagated by simple thermal conduction. In fact, the unburnt mixture gives rise to a displacement of gas in the tube, and if the constrictions are sufficiently near together the flame which passes the first ring is projected through the second and ignites the mixture in front of it, while the part which is situated between the two rings is still in combustion. It is owing to the projection of this 'tongue of flame' that the combustion of a relatively large volume of gas becomes extremely rapid. It is clearly shown that it is not a question here of a stable system similar to a true detonation. Kirby and Wheeler [30, 1931] have made similar observations in closed tubes with mixtures of air and methane (10%) or carbon monoxide (58%). The increase of velocity is less, but the phenomenon has the characteristics of a vibratory explosion. With carbon monoxide the sudden expansion resulting from the almost simultaneous combustion of the gas in the compartments limited by the constrictions gives rise to a shock wave which passes through the gases undergoing combustion at a velocity of 1,380 m. per sec., that is, at a velocity of the order of magnitude of an explosion wave.

3. Photographic records have sometimes been made in internal-combustion engines of flames propagated at very high velocities and seeming to attain the velocities of detonation. Withrow and Boyd [54, 1931] with a hydrocarbon-air mixture (75% of petrol and 25% benzene) have photographed a flame initially propagated at a mean velocity of about 20 m. per sec.; this velocity then increases to 35 m. per sec., and finally decreases to 10 m. per sec. When knock is produced, in consequence of advancing the spark, there is a moment when after the normal combustion of part of the gaseous mixture it is observed that the remainder suddenly burns in a time indeterminable from the photographs. This may occur either from a simultaneous ignition at every point where the mixture has not yet burnt, or by the propagation of an explosion wave whose velocity cannot be measured on the photographic records of Withrow and Boyd. The authors at first seem to have adopted this hypothesis. However, in a later paper Withrow and Rassweiler [55, 1933] no longer make mention of detonation, but only of a flame of high velocity preceded by spontaneous ignition.

The experiments of Duchêne [18, 1932] lead to results similar to those of the preceding authors and do not help towards a definite explanation. When knock was produced in his apparatus he obtained an auto-ignition which, he stated, immediately set up an explosion wave. He clearly proved, as did Withrow, that normal combustion is suddenly interrupted by an extremely rapid and very luminous form of propagation. This propagation travels (a great many times) from one end to the other of the vessel at a velocity of the order of that of the explosion wave. However, as a result of later experiments, the conception of Duchêne [19, 1935] has somewhat changed. He states: 'The explosion wave would be developed at a very high velocity; it would be too badly recorded on the photographs to be measured and the striations observed would only be those of a shock wave, following on detonation, which would be propagated a great number of times from one end to the other of the vessel at a velocity in the neighbourhood of 1,000 m. per second.'

The propagation of these shock waves cannot be doubted from the photographic records of Duchêne, but very possibly they may not be due to a true explosion wave, of which, as yet, the formation in an internal-combustion engine never seems to have been proved with certainty. In this connexion reference may be made to the discussion about the formation of the explosion wave. It seems proved, from experiments mentioned above, that in engines there may be phenomena propagated at velocities approximating those of an explosion wave. These phenomena may be due to the simultaneous ignition at different places of the gaseous mass, or to flames of very high velocity, or to shock waves of still higher velocities, causing or completing the combustion of the part of the mixture not yet burnt, and giving rise possibly to important mechanical effects. In order to determine precisely the true nature of these phenomena and their exact velocity further investigations are required.

REFERENCES

1. Andreeff, E. A. *Voien. Chim.* **3**, 13 (1933).
2. Berthelot, M. *Compt. rend.* **94**, 149 (1882).
3. Berthelot, M., and Vieille, P. *Comptes rendus*, **93**, 18 (1881), and **94**, 101 (1882). The works of Berthelot and of Berthelot and Vieille on detonation will be found in the following book by Berthelot: *Sur la force des matières explosives* (2 volumes), 3rd ed., Paris, 1883.
4. —— —— *Compt. rend.* **94**, 822 (1882).
5. Bone, B. A., and Fraser, R. P. *Proc. Roy. Soc., A*, **130**, 342 (1931).
6. Campbell, C. *J.C.S.* **121**, 2483 (1922).
7. Campbell, C., and Finch, A. C. *J.C.S.* 2094 (1928).
8. Campbell, C., King, A., and Whitworth, C. *J. Franklin Inst.* **28**, 681 (1932).
9. Campbell, C., Littler, W. B., and Whitworth, C. *Proc. Roy. Soc., A*, **137**, 380 (1932).
10. Campbell, C., Whitworth, C., and Woodhead, D. W. *J.C.S.* **59** (1933).
11. Campbell, C., and Woodhead, D. W. *J.C.S.* 1572 (1927).
12. —— —— *J.C.S.* **129**, 3010 (1926).
13. Chapman, D. L. *Phil. Mag.* (V), **47**, 90 (1899).
14. Chapman, W. R., and Wheeler, R. W. *J.C.S.* **138**, 2139 and 2927 (1926).
15. Dixon, H. B. *Phil. Trans., A*, **184**, 97 (1893), and **200**, 315 (1903).
16. Dixon, H. B., and Cain, J. C. *Mem. and Proc. Manch. Lit. Phil. Soc.* **38**, 174 (1893–4).
17. Dixon, H. B., Campbell, C., and Slater, W. E. *Proc. Roy. Soc., A*, **90**, 506 (1914).
18. Duchêne, R. *Bull. techn. aéron.* no. 11 (1932), and *Science aérienne*, **3**, 53 (1934).
19. —— Private communication (1935).
20. Dumanois, P. *Compt. rend.*, **186**, 292 (1928).
21. —— *Compt. rend.* **182**, 1378 (1926).
22. Dumanois, P., Mondain-Monval, P., and Quanquin, B. *Compt. rend.* 1158 (1931).
23. Egerton, A., and Gates, S. F. *Proc. Roy. Soc., A*, **114**, 152 (1927) and *A*, **116**, 516 (1937).
24. Garner, B. *Trans. Faraday Soc.* **26**, 590 (1930).
25. Gawthorp, D. B., Shepherd, W. C. F., and Perrott, G. St. J. *J. Franklin. Inst.* **211**, 67 (1931).
26. Hugoniot. *J. math.* iv, 3, 477 (1887), and *J. Éc. Polytech.* 57^e et 58^e cahiers (1887 and 1889).
27. Jones, R. H., and Bower, J. *Mem. and Proc. Manch. Lit. Phil. Soc.* **42** (1897–8).
28. Jouguet, E. *J. Math.* 347 (1905), and 6 (1906). The complete theory of the phenomena of detonation is assembled in the following book by Jouguet: *Mécanique des explosifs*, Doin éditeur, Paris (1907); see also *2^e Congrès Intern. de Mécanique Appl.*, Zürich (1926).

29. Jouguet, E. *Compt. rend.* **157**, 545 (1913). See also Crussard, L. *La Techn. mod.* **9**, 84 (1914).
30. Kirby, W. A., and Wheeler, R. V. *J.C.S.* 2303 (1931).
31. Laffitte, P. *Compt. rend.* **177**, 178 (1923), and **179**, 1394 (1924); see also *Ann. Phys.* x, **4**, 623 (1925).
32. —— *Compt. rend.* **186**, 951 (1928).
33. Laffitte, P., and Breton, J. *Compt. rend.* **199**, 146 (1934), and unpublished work.
34. Laffitte, P., and Dumanois, P. *Compt. rend.* **183**, 284 (1926).
35. —— —— *Compt. rend.* **186**, 146 (1928).
36. Laffitte, P., and Patry, M. *Compt. rend.* **191**, 1335 (1930); see also Patry, M. *Thèse*, Nancy (1933), Hermann éditeur, Paris (1933).
37. Le Chatelier, H. L. *Compt. rend.* **130**, 1755 (1900).
38. —— *Compt. rend.* **131**, 30 (1900).
39. Lewis, B. *J.A.C.S.* **52**, 3120 (1930).
40. Malinowski, A. E., Naugolnikow, B. N., and Tkachenko, K. T. *Phys. Z. Sowjet*, **5**, 446 (1934).
41. Mallard, E., and Le Chatelier, H. L. *Ann. Min.* **4**, 274 (1883).
42. Mason, W., and Wheeler, R. V. *J.C.S.* **117**, 47 (1920).
43. Moureu, C., Dufraisse, C., and Chaux, R. *Compt. rend.* **184**, 413 (1927); *Chimie et Industrie*, **17**, 531 (1927), and **18**, 403 (1927).
44. Muraour, H. *Compt. rend.* **194**, 280 (1932), and *Rev. gén. des sciences*, **44**, 567 (1933).
45. Payman, W. *Proc. Roy. Soc., A*, **120**, 90 (1928).
46. Payman, W., and Robinson, H. *Safety in Mines Research*, Paper no. 18 (1926).
47. Payman, W., and Shepherd, W. C. F. *Safety in Mines Research*, Paper no. 29 (1927).
48. Robinson, H., and Wheeler, R. V. *J.C.S.* 758 (1933).
49. Roux, G., and Sarrau, E. *Comp. rend.* **76**, 1089 (1873).
50. Semenoff, N. N. *J. Roy. Phys. Ch.* 241 (1928), and 4 (1933).
51. Sokolik, A., and Shtsholkin, K. *Phys. Z. Sowjet*, **4**, 795 (1933).
52. Wendlandt, R. *Z. phys. Ch.* **116**, 227 (1925).
53. White, A. G. *J.C.S.* 1159 (1928).
54. Withrow, L., and Boyd, T. A. *Ind. Eng. Chem.* **23**, 539 (1931).
55. Withrow, L., and Rassweiler, G. M. *Ind. Eng. Chem.* **25**, 1359 (1933).

SPECIFIC BEHAVIOUR OF FUELS AND DOPES

10. KNOCKING CHARACTERISTICS AND MOLECULAR STRUCTURE OF HYDROCARBONS

By WHEELER G. LOVELL, A.B., M.S., and JOHN M. CAMPBELL, B.S.

Research Laboratories Section, General Motors Corporation, Detroit

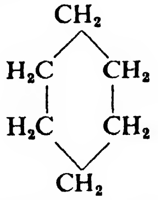
INTRODUCTION

INTEREST in the relation between the molecular structure of hydrocarbons and their knocking characteristics in an internal-combustion engine is of comparatively recent origin. Such interest arises from the fact that isomeric hydrocarbons may have very widely different tendencies to knock. As a result the utility of these isomeric forms when used in an internal-combustion engine is subject to a wide variation, because the knock has been an effective barrier to the use of higher compression ratios and hence to higher thermal efficiency of an internal-combustion Otto cycle engine. The potential power to be obtained on an engine operating at its maximum permissible compression ratio on one or another of two isomeric hydrocarbons may differ by as much as 50%.

Such isomers may be compounds which are easily distinguishable from one another as belonging to different hydrocarbon families such as the olefine, 1-hexene:

$$CH_2{=}CH{-}CH_2{-}CH_2{-}CH_2{-}CH_3,$$

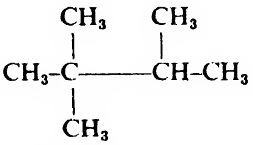
and the naphthene, cyclohexane, which has the same ultimate composition as represented by the formula C_6H_{12} but having the ring structure:



Other isomers may be of the same hydrocarbon family and distinguishable with some difficulty by the usual chemical methods of analysis and yet show extremely wide differences in knocking tendency. Such a pair of isomers are normal heptane and 2,2,3-trimethyl butane having the structures:

$$CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_3$$

and



$$CH_3{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}{-}\!\!-\!\!-\overset{\displaystyle CH_3}{C}H{-}CH_3$$

These two hydrocarbons represent two extremes in anti-knock quality. Under certain specified conditions normal heptane begins to knock at compression ratios below 3 to 1, while its isomer, 2,2,3-trimethyl butane, does not begin to knock until the compression ratio is raised to 13 to 1 [24, 1934]. Some conception of the magnitude of this difference may be gained from the observation that at 13 to 1, where one of these hydrocarbons just begins to knock, it would be physically impossible to operate with normal heptane due to the severity of detonation.

Such relationships between molecular structure and knock are not to be confined to the hydrocarbons themselves, but may also be considered from the standpoint of the hydrocarbons plus anti-knock agents such as lead tetraethyl, especially in view of the widespread use of this material in motor fuels. Lead tetraethyl has been found to be efficient in eliminating knock, varying over a wide range, depending upon the hydrocarbon fuel in which it is utilized. This effectiveness can also be related to the molecular structure of the fuel.

HISTORICAL

As early as 1920 Midgley [25] observed wide differences in the combustion of fuels in internal-combustion engines, not only among isomeric compounds containing carbon, hydrogen, and oxygen, but also wide differences in the combustion or the knocking characteristics of different chemical classes of hydrocarbons. In 1921 Ricardo [29] published the results of investigations on the highest useful compression ratio of a number of hydrocarbons and found wide differences between the values of different internal-combustion engine fuels in this respect. In 1922 Midgley and Boyd [26] published data on the detonation characteristics of various mixtures of aromatic and paraffin hydrocarbons.

Edgar [8], in 1927, suggested the use of *n*-heptane and 2,2,4-trimethyl pentane mixtures as standards for rating fuels for knock. The straight-chain paraffin hydrocarbon *n*-heptane was very prone to knock, while the branched-chain *iso*-octane was comparatively free from knock, and it was thus apparent that different isomeric heptanes and octanes would have greatly differing tendencies to knock. In 1929 Birch and Stansfield [2] and Nash and Howes [27] published data on the knock-rating of solutions in gasoline of several different hydrocarbons.

In 1931 Lovell, Campbell, and Boyd published [20, 21] data on an extended series of pure paraffin and olefine hydrocarbons in fairly dilute solutions in gasoline, showing a number of consistent and regular relationships between the molecular configuration or their conventional structural formula and the tendency of these fuels to knock as measured in dilute solution in gasoline.

More recently the determinations of Garner, Wilkinson, and Nash [12, 1932] on the olefines, and Garner and Evans [11, 1932] on naphthene and aromatic hydrocarbons have been published. Hoffman, Lang, Berlin, and Schmidt [16, 17, 1933] presented data on a considerable number of hydrocarbons of different classes. Recently also, Lovell, Campbell, and Boyd [22, 1933; 23, 1934] published data on a large number of naphthene and aromatic hydrocarbons. These data have related to the behaviour of the compounds in solutions in gasoline of the range of 10 to 20%.

Data on the behaviour of various hydrocarbons in the pure state are not so extensive, although Lovell, Campbell, and Boyd [24, 1934] have given data on a series of about 100 hydrocarbons in terms of compression ratio.

Most of the data in the literature pertain to the knocking characteristics of the hydrocarbons when measured under different engine conditions in fairly dilute solutions up to about 20% at a maximum. Much of the data have been expressed in terms of octane number of the solutions, and recently Garner, Evans, Sprake, and Broom [13, 1933] have published a compilation of the data available up to 1934 in terms of 'blending octane number'. The 'blending octane number' of a hydrocarbon is an extrapolated value and does not necessarily bear any relation to the actual octane number of this material when tested in the pure state, but is an extremely useful concept for practical purposes of computing the relative anti-knock value of different hydrocarbons in solution.

The data upon the effectiveness of lead tetraethyl as a knock suppressor as related to the fuel in which it is used are mostly of fairly recent date. In 1932 Garner, Wilkinson, and Nash [12] found that the effectiveness of lead tetraethyl in increasing the octane number of 20% solutions of several alpha olefines in a base fuel increased with the molecular weight from pentene through nonene. Similar data were also obtained by Garner and Evans [11, 1932] on 21 hydrocarbons, including aromatics, cyclohexanes, and cyclopentanes, also in 20% solutions; and they concluded that the order of increasing effectiveness was aromatics, cyclohexanes, and cyclopentanes, as measured in these solutions. Alden in 1932 [1] and Hebl, Rendel, and Garton in 1933 [15] presented data on the effectiveness of lead in a variety of gasolines. More recently, Campbell, Signaigo, Lovell, and Boyd [7, 1935] have given data on about 60 pure hydrocarbons, comparing the effect of definite additions of lead tetraethyl on the critical compression ratios of these materials. The wide range of the effectiveness of the lead, extending from positive to negative values, appeared to be closely related to the structure of the hydrocarbon, large differences appearing even between isomers of a class.

METHODS OF MEASURING KNOCKING CHARACTERISTICS OF HYDROCARBONS

In order to evaluate the relative tendencies to knock of different hydrocarbons, a number of methods have been used. The methods have been subject to a large amount of change and development, and especially so because the development of methods of rating fuels for knock, in general, has been contemporary with the rating of pure hydrocarbons. (See Art. 15.)

It was recognized at the outset that the evaluation of the knocking characteristics of hydrocarbons could not be accomplished by analytical methods or by testing the knocking behaviour of a mixture of hydrocarbons and then determining the composition of the mixture [9, 1926; 33, 1927]. This is due to the complexity of most fuels and to the lack of suitable analytical methods, and especially methods for analysing mixtures of isomers which may have wide differences in tendencies to knock. Accordingly, it has been necessary to obtain hydrocarbons of known purity and definite structure prepared synthetically and then to test them, either in the pure state or in known concentrations in other fuels.

Various methods have been used for testing; and at present all methods known to be reliable are based on burning the fuel in an engine. This is due to the fact that the mechanism of knock is not sufficiently well understood to permit simplification or duplication of the essential conditions of combustion outside of an actual engine.

Since the knock is a function of both engine conditions and of fuel, measurements have been made in terms of engine conditions such as, for example, the compression ratio which could be used with the pure hydrocarbon or a definite mixture for a fixed degree of knock. Since different engines are not directly comparable, attempts have been made to cancel out the effect of the engine by matching the hydrocarbon, or mixture, with a standard fuel whose knocking characteristics could be varied by suitable changes in its composition. However, since two fuels may knock alike in one engine but not in another, this method does not completely eliminate the effect of engine conditions or permit absolute standardization, nor does it necessarily permit translating the units of one scale directly to another. However, these effects are usually small in comparison with the differences between many hydrocarbons.

Fuels used as standards of comparison have been quite varied and have included mixtures of benzol, tetraethyl lead, or aniline (all acting to suppress knock although in widely differing degrees of effectiveness) with gasoline; mixtures of benzene and *n*-heptane, and mixtures of *n*-heptane and *iso*-octane (representing the octane number scale) have also been used [4, 1931; 5, 1928; 6, 1930].

The concentration in which the hydrocarbon is tested is also important. As previously mentioned, some of the hydrocarbons have been examined in a pure condition, but this method has a number of serious disadvantages. A very practical one has to do with the difficulty of securing large enough supplies of the hydrocarbons to operate even a single-cylinder engine for a suitable length of time; and

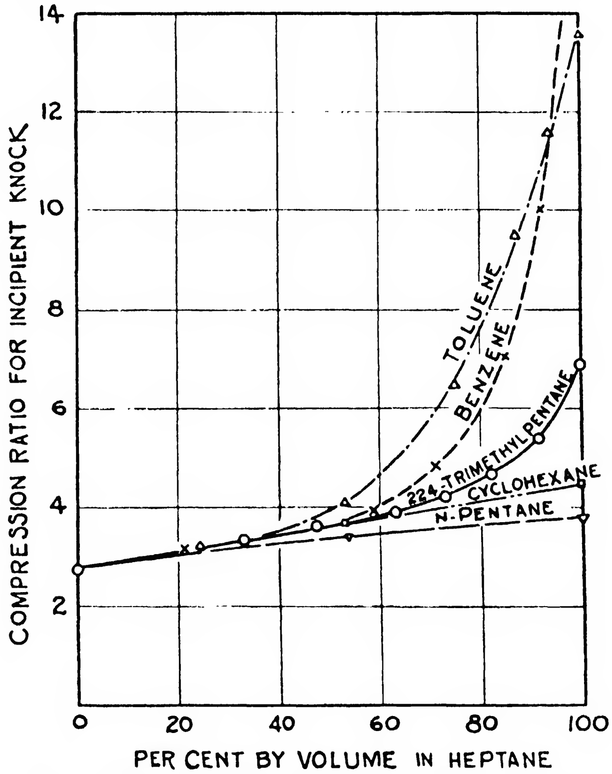


FIG. 1. Knocking characteristics of two component mixtures of hydrocarbons.

this is especially serious when the hydrocarbons must be prepared by laboratory methods. An early difficulty with the use of pure undiluted hydrocarbons was the enormous range of knocking characteristics to be covered, ranging from compression ratios above 15 to below 3, and an additional complication is the enormous range of volatility which must be dealt with to make tests in a carburettor-type engine.

Accordingly, a good deal of the data in the literature have been reported in terms of fairly dilute solutions, ranging from 10 to 30%, and in various base gasolines. Pure *n*-heptane has also been used to a limited extent. The concentrations used have been expressed in terms of weight and also volume per cent., and also in terms of gram molecules per litre of solution. The choice of concentration to be used is quite important, since the change in the knock-rating with concentration is not necessarily a regular or a linear relationship. This is illustrated in Fig. 1, taken from data presented by Campbell, Lovell, and Boyd [5, 1928]. In plotting the change in compression ratio which results when various concentrations of the different hydrocarbons are added to normal heptane, it is to be seen from Fig. 1 that the curves are by no means straight lines. In other words, the changes in the knocking characteristics of a fuel upon addition of a hydrocarbon are not always proportional to the amount of material added. This same observation was made by Thornycroft and Ferguson [34, 1932]. It is consequently to be expected that the relative knocking behaviour of hydrocarbons as measured in dilute solutions will not necessarily be exactly similar to that determined with the pure compounds.

KNOCKING CHARACTERISTICS OF HYDROCARBONS

For simplicity in considering the knocking characteristics of hydrocarbons, especially with relation to their molecular structure as revealed by the conventional structural formula, the behaviour in dilute solution may well be considered first, especially as they seem to give a key to the whole series of relationships. After this, the relationships as revealed by the available data on the behaviour of hydrocarbons as tested in the pure state will be discussed. Since the relative behaviour of these materials depends to a certain extent, as has previously been indicated, upon the experimental conditions used for their evaluation, a brief summary of such data will be given. Finally, the data on the effectiveness of lead tetraethyl in eliminating the knock in hydrocarbons of various structures will be summarized.

The data upon all of the hydrocarbons as reported by different investigators will be found tabulated for each hydrocarbon in the tables at the end, to which reference is made for an explanation of the various units of measurement used, and for the agreement of the values as reported by different investigators.

HYDROCARBONS IN DILUTE SOLUTION

In considering these relations between knocking behaviour in dilute solution and chemical structure, the authors have used the so-called aniline equivalent scale, which represents, in terms of aniline, a knock suppressor, the knock effect of the hydrocarbon when measured in a solution of 1 gram molecule per litre of solution in a reference gasoline, or as many grams per litre as there are units in the molecular weight of the hydrocarbon. The use of this molecular basis thus makes it unnecessary to interpolate or extrapolate the original data and also has the important advantage of making available for unified treatment a larger body of data than might otherwise be readily possible.

Paraffin Hydrocarbons

The paraffin hydrocarbons comprise probably the simplest class to deal with, since the number of isomers boiling within the gasoline range, although very large, is still much smaller than the numbers of isomers of olefine, naphthene, or aromatic hydrocarbons of similar boiling ranges.

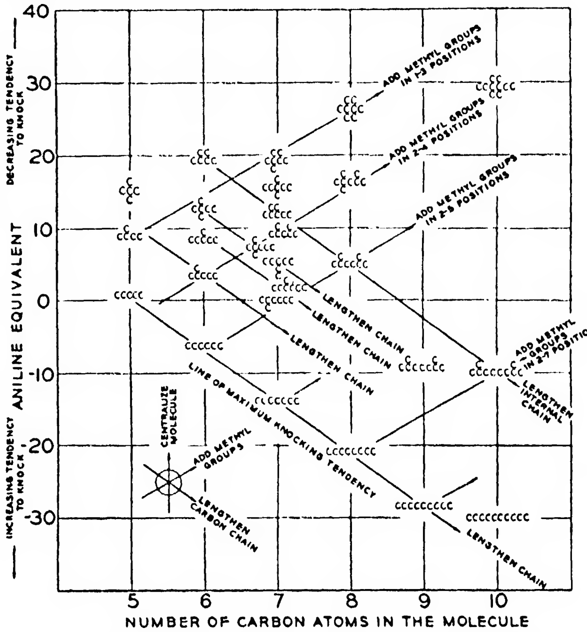


FIG. 2. Aniline equivalents of paraffin hydrocarbons.

A graphical representation in terms of aniline equivalents is given in Fig. 2. The aniline equivalents are plotted as ordinates and the number of carbon atoms in the molecule as abscissae. The values for the different compounds are plotted as points, and the particular hydrocarbon is indicated by a partial structural formula near the point. In these formulae, only the carbon atoms are represented, but they are grouped as in the conventional structural formula. Thus, for example,

$$\begin{array}{ccccccccc} & & C & & C & & & & \\ & & | & & | & & & & \\ C & - & C & - & C & - & C & - & C \end{array}$$ represents 2,3-dimethyl pentane

and C–C–C–C–C represents *n*-pentane.

These data as plotted show a number of interesting relationships, most of which are indicated by the appropriately designated lines.

(1) For the normal or straight-chain paraffin hydrocarbons there appears to be a regular increase in tendency to knock with increase in the length of the carbon chain in the molecule, or with the molecular weight. This increase in tendency to knock with an increase in the length of the unbranched carbon chain appears to be quite a general relationship, and it appears also in the case of the hydrocarbons having a 2-methyl group, a 3-methyl group, or a 2,2-dimethyl group. Also, even the lengthening of the unbranched carbon chain, when this chain is in the interior of the molecule, produces a similar result. It is also possibly

significant that, upon this molecular basis, the lengthening of the unbranched carbon chain produces a substantially constant increase in tendency to knock per carbon atom.

(2) On the other hand, the successive addition of methyl groups to a carbon-atom chain results in a decreased tendency to knock. This branching of the chain by the successive addition of methyl groups also appears to be a regular relationship in that the addition of a methyl group accompanies a fairly definite increase in anti-knock value or decrease in tendency to knock.

(3) It is also possible to consider the data represented graphically in Fig. 2 as the relationships between isomers of a definite number of carbon atoms. In general, for a given molecular size, as that is loosely termed the centralization of the molecule is increased, there is less tendency to knock. It is difficult to define this concept of centralization of a molecule quantitatively, but it may be described in a general way as a more compact arrangement of the structural formula of the molecule.

(4) It follows from these concepts of the consistencies between molecular structure as revealed by the conventional structural formulae that when the number of carbon atoms in a molecule is increased, the anti-knock value may either increase or decrease, and that the greater the number of carbon atoms in a molecule the greater the range in knocking characteristics between the best and the worst knocking compound. It is, consequently, difficult to classify paraffin hydrocarbons as a class as being either good or bad from the standpoint of knock, since it depends upon which particular isomers are to be considered.

Straight-Chain Olefine Hydrocarbons

The range of knocking qualities exhibited by the olefine hydrocarbons is, as might be expected from the previous consideration of the paraffins, also very great. Aside from the effect of the carbon-atom skeleton itself, the position of the double bond in the molecule is also of great importance in relation to the knocking characteristics of these materials. This is revealed by the data on the straight-chain olefine hydrocarbons.

These data are shown in a graphical form in Fig. 3, representing the data on the aniline equivalents, and the relationship of the molecular structure of these compounds to the knocking characteristics is especially evident from this graphical portrayal.

(1) The effect of lengthening the carbon chain unbroken by a double bond appears to be entirely similar to that previously observed in the case of the paraffins and of a similar quantitative amount, as indicated on the chart by the lines parallel to that for the *n*-paraffins. Lengthening the unbroken carbon chain increases the tendency to knock or decreases the aniline equivalent.

(2) The effect of the position of the double bond is shown clearly by a consideration of the isomers of a given number of carbon atoms. In these straight-chain olefines, as the double bond is progressively nearer to the centre of the molecule, the tendency to knock decreases by fairly regular steps.

(3) Upon this molecular basis it is also interesting to note that the knock of these compounds appears to be determined by the longest unbroken straight carbon chain, and this appears to be so practically irrespective of the size of the molecule, within the limits covered by these data.

(4) As a class the straight-chain olefines all appear to be superior, from the knock standpoint, to the corresponding paraffins. However, there are, of course, branched-chain paraffins which are superior to even the best of the straight-chain olefines. Consequently, no simple conclusions can be drawn as to the general superiority of one of these classes of compounds as compared with the other.

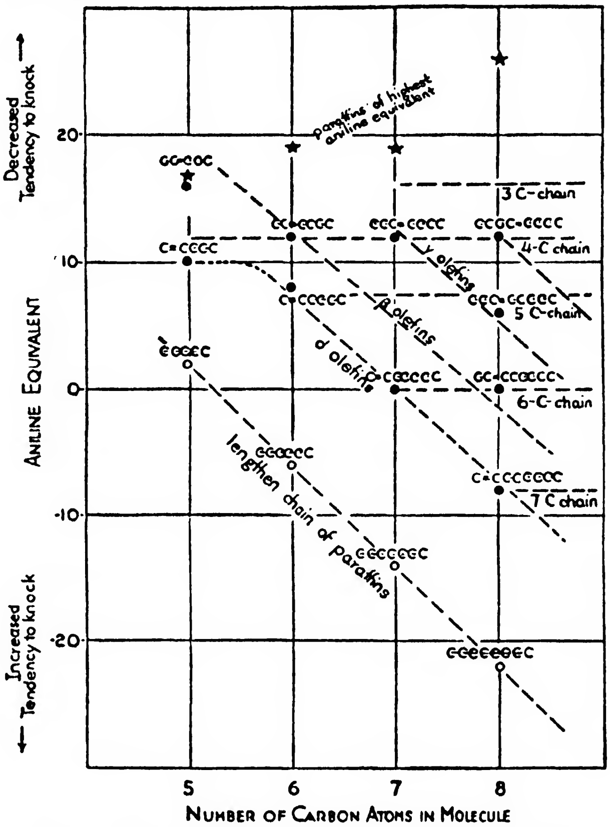


FIG. 3. Detonation characteristics of straight-chain olefines.

Branched-Chain Olefine Hydrocarbons

Olefines with branched chains are of special interest, as they represent the structural condition of a double bond combined with a varied branched structure. The position of the ethylene linkage doubtless affects the knocking characteristics, as was found to be the case for the straight-chain olefines; and by analogy with the paraffins the branching of the structure should also be of great influence. The data available at present does not permit of a general picture of this type of compound because of the very large number of possible isomers.

The available data, however, may be summarized graphically as shown in Fig. 4, where the knocking characteristics of the branched-chain olefines, as given by the aniline equivalents as before, have been plotted vertically, with the values for the corresponding saturated compounds also represented by the circles at the bottom of the dotted lines, so that the specific effect of the double bond in the molecule is especially evident.

A number of interesting regularities appear in the data:

(1) All of these unsaturated hydrocarbons show greater aniline equivalents or a greater anti-knock value than the corresponding saturated paraffin compounds. The differences do not appear constant. By analogy with the straight-chain olefines, it might be expected that the greatest difference would accompany the introduction of a double bond so as to break up a long chain of CH_2 groups, and there is some qualitative indication that this is frequently so.

(2) It is to be expected that an olefine corresponding to a paraffin of high aniline equivalent would also be a compound of high aniline equivalent, and this seems to be borne out by the available data. Within the limits of the data the best olefine of a given number of carbon atoms is probably better in anti-knock value than the best paraffin. However, in general, the two classes of olefines and paraffins appear to cover about the same range of anti-knock value.

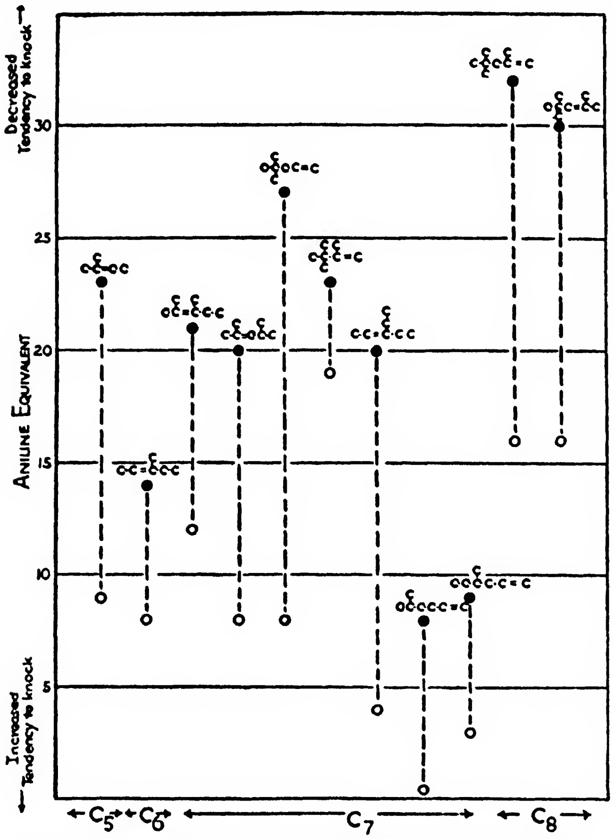


FIG. 4. Detonation characteristics of branched-chain olefines.

Cyclohexane Hydrocarbons

The family of cyclic hydrocarbons, exclusive of those containing a benzene ring, is of considerable interest in respect to knocking characteristics, not only because of the presence in considerable amount of many of these compounds in commercial fuels, but also because of the many varieties of isomerism which may exist and which may greatly affect their behaviour in the engine as regards knock.

Compounds containing the cyclohexane ring have been investigated to a considerable extent as represented by over 30 individual compounds. The values as recorded in the appendix are represented graphically in Fig. 5, in which the aniline equivalents have been used as the basis of comparison. A number of general relationships appear from these data on the cyclohexane hydrocarbons.

(1) Cyclohexane itself has superior anti-knock quality to *n*-hexane; the closure of the ring apparently enhances this quality.

(2) The presence of an unbranched side chain results in a decrease in aniline equivalent, and its lengthening appears to be a regular and progressive change and of a magnitude similar to that previously observed with the paraffin hydrocarbons. The relation holds not only for the lengthening of a straight side chain on cyclohexane itself, but also on methyl cyclohexane. In fact, this relation appears to be so general as to include lengthening of the carbon chain of a branched side chain, which results, approximately quantitatively, in a similar decrease in anti-knock value.

(3) The effect on knock of branching a side chain appears to be very great. A cyclohexane hydrocarbon with highly branched or centralized side chain may be very much superior in anti-knock value or aniline equivalent upon a molecular basis to the parent cyclohexane itself.

(4) The effect of position isomerism on the knocking characteristics of the cyclohexane hydrocarbons appears to be very small for the compounds upon which data are available, and while the differences in knock between cyclohexane derivatives with side chains on adjacent or non-adjacent carbon atoms may be appreciable, it does not at present appear to be very significant.

(5) Another type of isomerism is that in which the side-chain carbon atoms have a different distribution between the chains. In general, it seems to be that a centralization of the molecule, or the distribution of the side-chain carbon atoms into a greater number of shorter chains, increases the anti-knock value of the hydrocarbon. However, the centralization of the single side chain itself in some cases increases the aniline equivalent much more than does redistributing the atoms among the different side chains.

(6) Comparing paraffins and cyclohexane hydrocarbons having the same number of carbon atoms, the cyclohexanes appear to be within the range of anti-knock quality that is established by the paraffins, and on the whole the range covered by these classes of hydrocarbons seems to be approximately the same.

Cyclopentane Hydrocarbons

The knocking characteristics of the cyclopentane hydrocarbons are not represented by nearly as many individuals as are the cyclohexane hydrocarbons. However, as far as is known, these two classes are quite similar to each other in the respect to which changes in the structure affect the knocking properties. Upon the molecular basis, cyclopentane itself is superior to *n*-pentane, and superior to cyclohexane. The seven carbon-atom ring, cycloheptane, is lower in anti-knock value than cyclohexane. Data upon the cyclopentane hydrocarbons are shown graphically in Fig. 6.

Cyclohexene Hydrocarbons

Those hydrocarbons containing a single double bond in a six-membered ring also have many points of similarity to the saturated cyclohexane hydrocarbons with a few exceptions, as far as is known at present.

The data on these cyclohexene hydrocarbons, as represented by over 20 compounds, is given graphically in Fig. 5 together with the corresponding saturated hydrocarbons for comparison, so as to permit of some generalizations upon the relation of their structure to the knocking characteristics.

(1) The lengthening of the unbranched side chain attached to the ring results in a progressive decrease in anti-knock value. However, it is worthy of note that methyl cyclohexene and also the dimethyl cyclohexenes are much superior as far as knock is concerned to cyclohexene itself. On the other hand, the addition of one or even two methyl groups to the cyclohexane ring resulted in a decrease in anti-knock value.

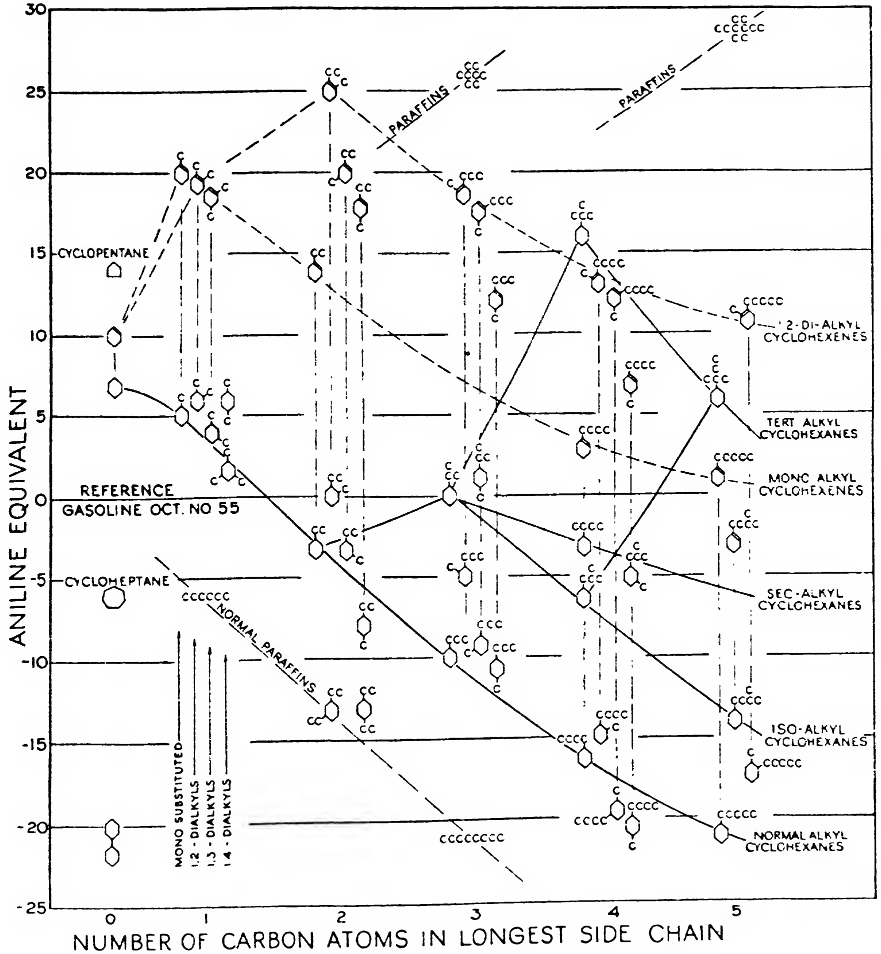


FIG. 5. Naphthene hydrocarbons having six-carbon ring.

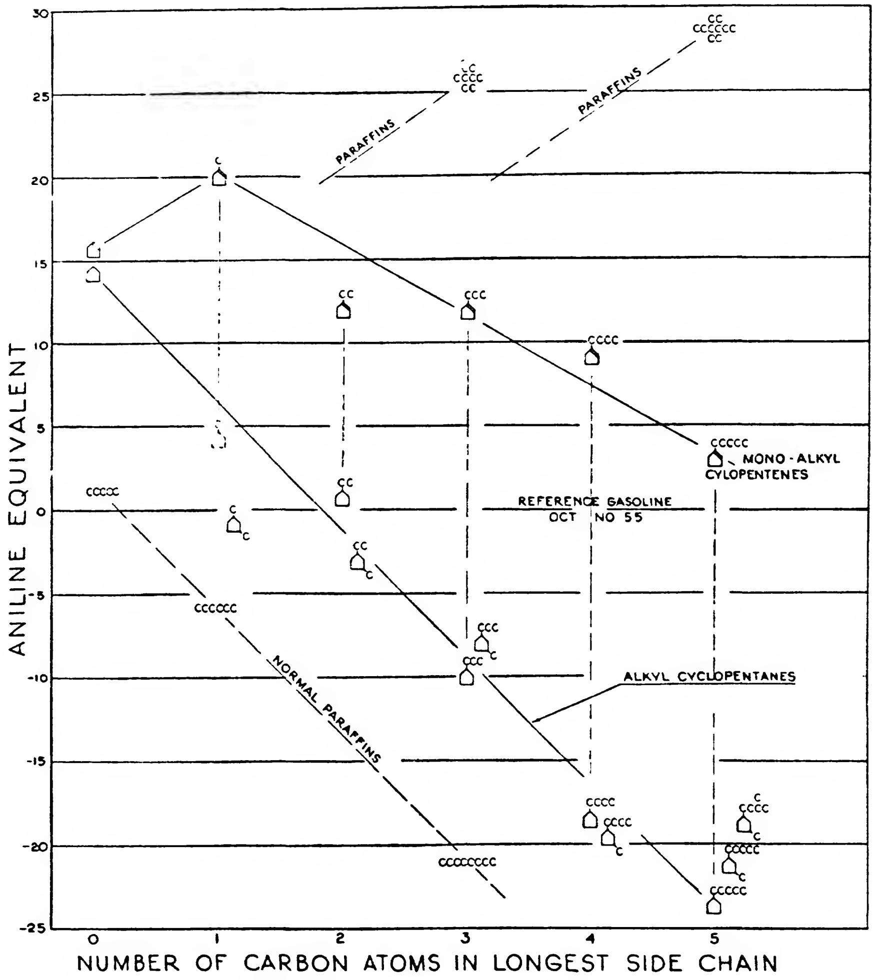


FIG. 6. Naphthenes with five-carbon ring.

(2) The effect of position isomerism for the cyclohexene hydrocarbons appears much greater than in the corresponding cyclohexanes. It is possible, of course, that this may be related to the relative position of the double bond in the ring. As far as is known, the isomers in order of decreasing anti-knock value are arranged 1–2, 1–3, and 1–4 in general, the 1–4 being inferior to either the 1–2 or the 1–3 isomers.

Cyclopentene Hydrocarbons

As far as is known, the cyclopentene hydrocarbons have much the same general behaviour as the cyclohexenes. The data on the compounds is shown in Fig. 6, which also shows the cyclopentanes for comparison.

In general, these unsaturated cyclic compounds are, as can be seen, superior to the corresponding saturated compounds, and the progressive lengthening of a single straight side chain decreases their anti-knock value. Exhibiting a behaviour similar to that observed in the cyclohexene series, methyl cyclopentene is superior to cyclopentene itself.

Aromatic Hydrocarbons

Aromatic hydrocarbons, as typified by benzene and toluene, were early recognized as superior compounds in respect to their tendency to knock in an engine. This class of compound has been extensively investigated, and the knocking characteristics of over 50 individual compounds have been measured, and a number of them by different investigators whose data appear to be in good agreement in general, especially in view of the fact that many of these compounds are quite sensitive to engine conditions.

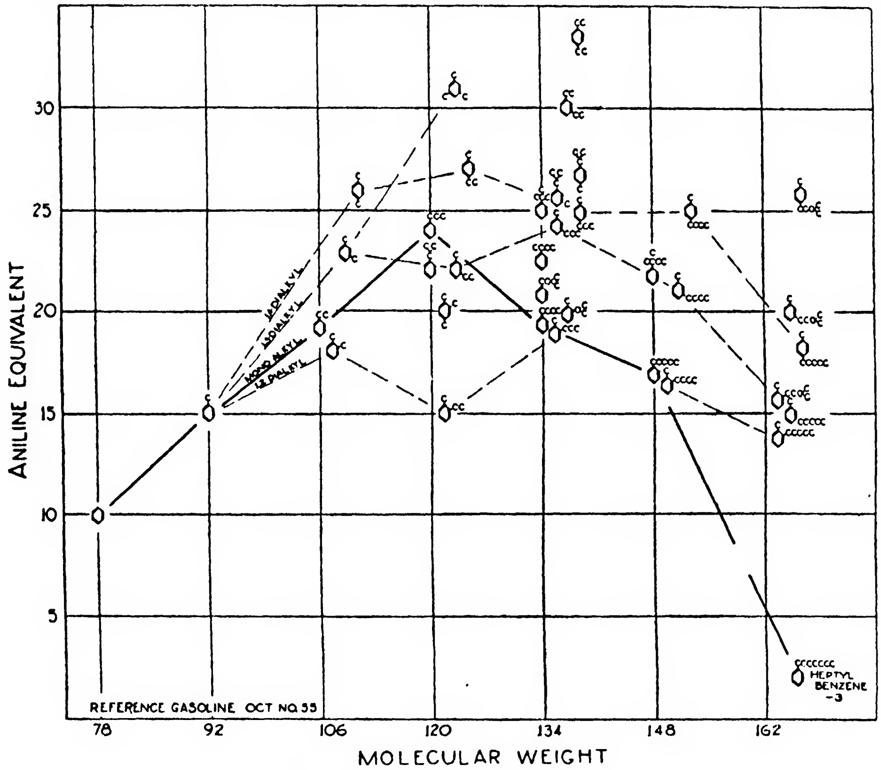


Fig. 7. Aromatic hydrocarbons.

Fig. 7 is a graphical representation of the data in terms of aniline equivalents, and from this a number of the general and more consistent relationships between molecular structure and knock become especially apparent.

(1) The addition of a progressively lengthened straight saturated side chain to the benzene nucleus results in a progressive increase in anti-knock value up to *n*-propylbenzene with a carbon chain-length of 3. Further increase in the length of the side chain results in a progressive lowering of the aniline equivalent. *n*-heptylbenzene, on a molecular basis, is only slightly better than *n*-hexane. Thus it appears as if after the straight alkyl side chain has reached a certain length, its lower anti-knock character begins to weigh against the anti-knock effect of the benzene nucleus and further increases in length of the alkyl side chain finally overcome the anti-knock effect of the benzene ring.

(2) Addition of methyl groups to the benzene nucleus results in a progressive increase in aniline equivalent. Thus toluene is higher in anti-knock quality than benzene, the xylenes are higher than toluene, and mesitylene is higher than the xylenes on a molecular basis.

(3) Position isomerism appears to exert a considerable effect on anti-knock quality as represented by the data on the xylenes and methyl-ethyl benzenes, and the compounds fall in order of increasing anti-knock values: ortho, meta, and para.

(4) Branching of the side chains containing more than three carbon atoms resulted in an appreciable increase in aniline equivalent. This is consistent with the previously observed behaviour of the paraffin and naphthene hydrocarbons.

(5) For these aromatic hydrocarbons, among compounds of given molecular weight, the anti-knock value varies with the distribution of the carbon atoms in the side chains and is probably related to the relative positions of the different side chains.

(6) The aromatic compounds as a class appear on this basis to be distinctly superior to the paraffins, in that they are all better than the worst paraffins. However, there are paraffin hydrocarbons that have an anti-knock effectiveness, as measured in aniline equivalents, about the same as the best of these aromatic compounds. In addition, it should be borne in mind that the measurements upon which such comparisons are based pertain to rather dilute solutions in gasoline and to conditions of engine operation which approximate those, now generally known as the 'Research' method. For details of the 'Research' method see article on knock measurement (Article 15).

Some other compounds somewhat akin to the aromatics are also of interest in these relations. Compounds containing the cyclopentadiene ring appear to have high anti-knock value, and dimethylfulvene with an aniline equivalent of 61 has the highest anti-knock value recorded in the literature for a pure hydrocarbon. Cyclohexadienes also have fairly high anti-knock value.

IN THE PURE STATE

As has been indicated previously, the relative knocking characteristics of hydrocarbons determined in dilute solution with a gasoline or another basic reference fuel do not necessarily correspond to the relative knocking characteristics of the same compounds as determined in the pure state. However, most of the general rules for correlation within a given class of compounds seem to be valid for both conditions.

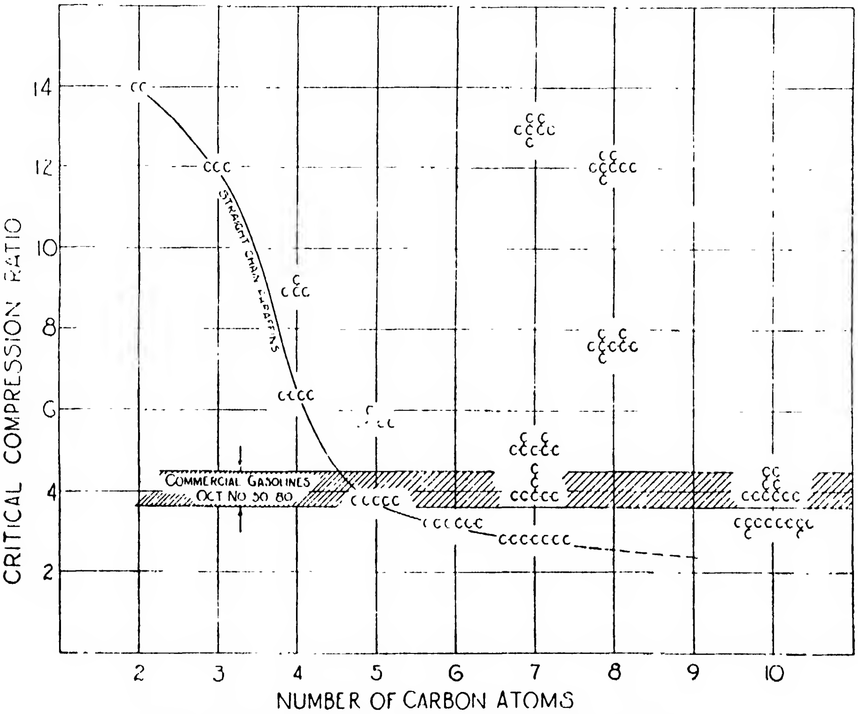


FIG. 8. Critical compression ratios of some paraffin hydrocarbons.

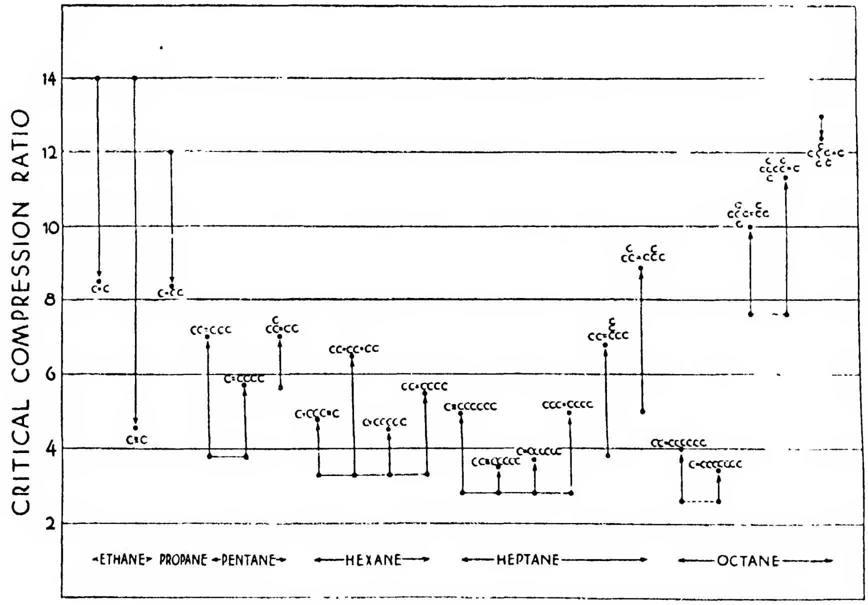


FIG. 9. Critical compression ratios of some olefine hydrocarbons.

In discussing these correlations for the determinations made on compounds in the pure state, it is convenient to divide the hydrocarbons into classes, much as before, and consider the classes separately. Most of the data have been taken from the publication of Lovell, Campbell, and Boyd [24, 1934], as expressed in terms of compression ratio for incipient knock under certain specified conditions.

Paraffin Hydrocarbons

The data on the paraffin hydrocarbons are represented graphically in Fig. 8, in which critical compression ratios are plotted against molecular weights for the hydrocarbons of structure indicated by the abbreviated formulae. This figure clearly shows the increasing tendency to knock with increasing length of the straight carbon chain. The paraffin having the least tendency to knock was methane. Increasing the length of the carbon chain abruptly increased the knocking tendency as shown by the steep slope of the curve down to *n*-pentane. Further increases in the length of the carbon chain resulted in appreciable but less abrupt changes in knocking tendency.

Fig. 8 also shows the powerful influence of more compact space arrangement of the carbon atoms to produce decreased knocking tendency. The critical compression ratios of the heptanes vary from 2·8 for *n*-heptane to 13 for 2,2,3-trimethylbutane. It is thus evident that some of the paraffin hydrocarbons have extremely high anti-knock properties.

Unsaturated Aliphatic Hydrocarbons

The data on the unsaturated aliphatic hydrocarbons are represented graphically in Fig. 9. This representation shows the critical compression ratios of the hydrocarbons of the structure indicated; there are also represented for comparison the compression ratios of the corresponding saturated compounds, as indicated by the origin of the vertical arrows.

Usually the unsaturated compound has a higher compression ratio than the corresponding paraffin, but there are notable exceptions to this in the case of ethylene, acetylene, and propylene, whose compression ratios are much lower than the corresponding saturated compound, the difference being almost 10 ratios in the case of acetylene. The position of the unsaturated linkage appears to be of considerable importance, and the specific effect of a double bond appears to increase as its location is moved towards the centre of the molecule. However, in the case of the straight-chain heptynes the effect of moving a triple bond towards the centre of the chain appears to be the opposite of that obtained in the case of the double bond. Centralization of two double bonds increases the compression ratio in the case of the hexadienes.

Naphthenes and Aromatics

A graphical representation of the relative knocking behaviour of aromatic and naphthenic hydrocarbons is given in Fig. 10. A number of interesting relationships between molecular structures and knocking tendencies of these hydrocarbons may be seen:

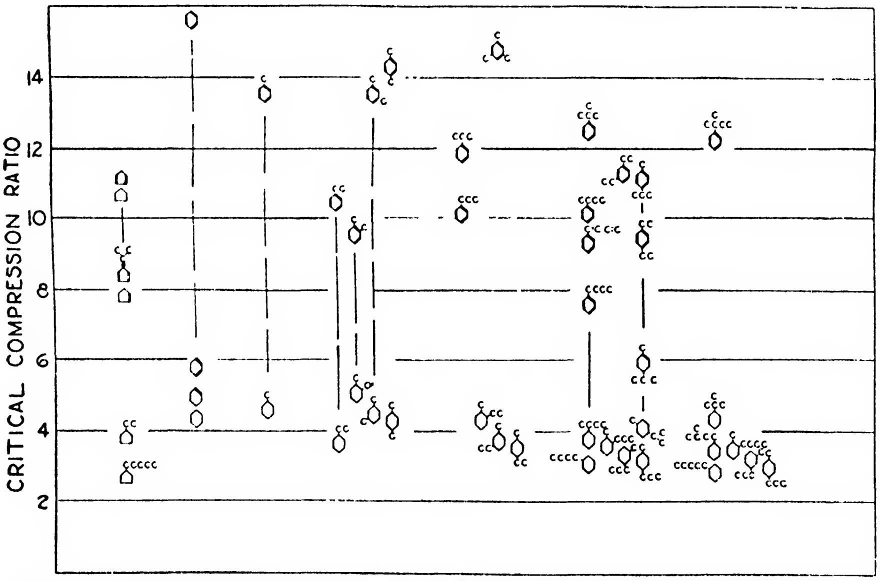


FIG. 10. Comparison of critical compression ratios of naphthenic and aromatic hydrocarbons.

1. The saturated cyclic hydrocarbons have distinctly greater knocking tendencies or lower critical compression ratios than the corresponding aromatic hydrocarbons.
2. The cyclohexane derivatives are comparable with commercial gasolines in knocking tendency for the most part.
3. Although two and three double bonds within the ring exert a strong anti-knock effect, a single double bond produces comparatively little effect. Cyclopentene, in fact, had a lower compression ratio than cyclopentane, although this was an exceptional case.
4. Increasing the length of the side chain increases the tendency to knock among both the aromatics and naphthenes.
5. Branching of the side chain produces a decrease in knocking tendency both among naphthenes and aromatics.

EFFECT OF ENGINE CONDITIONS

A large proportion of the more extensive data on the knocking characteristics of different hydrocarbons, and most of the data reported as aniline equivalents, were obtained under conditions of engine operation corresponding to the conditions at present generally known as the 'Research' method. The determinations made under conditions of higher engine speed, mixture temperature, or jacket temperature indicate that the values may vary appreciably between the different conditions, as shown in specific cases by the data given in the tables.

In terms of aniline equivalents, the relatively few data indicate that the aromatic hydrocarbons, as a class, are more susceptible to changes in engine conditions than other classes of hydrocarbons. The data also indicate that the relative knocking characteristics of two hydrocarbons, even of the same class, may vary somewhat with varying engine conditions.

The more extensive data of Garner and associates [13, 1933] on the effect of jacket temperature indicate that in the case of the naphthenes and *n*-paraffins the value (in terms of blending octane number) obtained at the higher jacket temperature is lower for the first members of the series, but that as the length of the carbon chain increases, the drop becomes smaller and eventually, at about the C_8 member, the relation becomes reversed. The higher olefines also appear to have lower anti-knock value when measured at the higher jacket temperatures. It is to be recognized, therefore, that all of these relations are based upon the comparison of one fuel with another under certain arbitrary engine conditions and do not represent absolute values applicable to all engines and all conditions. Usually, however, the differences in relative values obtained under different conditions appear to be small in comparison with differences which have been observed between some different hydrocarbons and between some isomers.

EFFECTIVENESS OF LEAD TETRAETHYL IN HYDROCARBONS

As has been indicated previously, the widespread use of lead tetraethyl as an anti-knock agent in motor fuels has led to a consideration of its relative effectiveness in suppressing knock in different hydrocarbons as a matter of considerable importance. A considerable amount of data has been published on this matter, for the details of which reference may be made to the individual values tabulated in the appendix.

Something of a general view of the range of magnitude of the effects may be obtained from Fig. 11. In this figure the critical compression ratios of most of the hydrocarbons have been plotted against the effectiveness of lead in these materials (expressed as the change in the critical compression ratio accompanying the addition of 1 c.c. per gallon). For convenience, the compounds are separately identified as saturated paraffins and naphthenes, alpha-olefines, diolefines and acetylene compounds, other aliphatic olefines, and, finally, unsaturated cyclic compounds. Lines have been drawn on the chart passing roughly through the points of most of these different classifications, but it is to be recognized that these lines do not necessarily represent functions, nor do they necessarily have any absolute significance. There has also been indicated an area representing an approximation of the location on such a chart of present commercial gasolines.

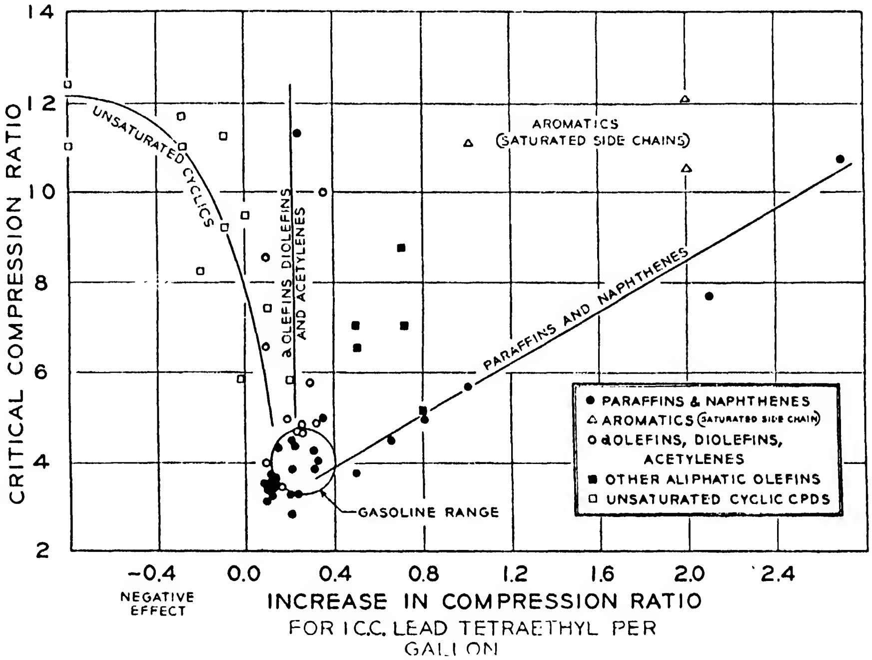


FIG. 11. Relative anti-knock effect of lead tetraethyl in different types of hydrocarbons.

The line drawn roughly through the paraffin and naphthene hydrocarbons may indicate that compounds of higher anti-knock value as measured in terms of critical compression ratio are materials in which lead is progressively more effective.

However, the line drawn through the compounds classified as alpha-olefines, diolefines, and acetylene compounds is substantially vertical. In other words, the effectiveness of lead in these compounds is substantially constant irrespective of the critical compression ratios of the hydrocarbons under consideration. The location on the chart of the other olefines appears midway between the alpha-olefine line and the paraffins, so that there appears no very direct relationship between critical compression ratio and lead effectiveness.

Of special interest are certain unsaturated cyclic compounds, including cyclopentadiene derivatives and certain aromatic compounds with unsaturated side chains. A line showing the general location of these hydrocarbons indicates a progressive lowering of the effectiveness of lead in them as the critical compression ratio of the compound increases. With a considerable number of these hydrocarbons, in fact, lead has a 'negative' effect; that is to say, the lead tetraethyl acts as a knock-inducer, and the critical compression ratio of the hydrocarbon is lowered by the addition of the lead.

The few aromatic compounds which were investigated are shown on the upper right of the chart, and they appear as compounds in which lead is very effective.

It is also of interest to consider the relationships of structure and lead effectiveness in the compounds more directly, and a view of these may be obtained from the data presented graphically in the other figures. Fig. 12 shows the data obtained on the aliphatic double- and triple-bonded compounds, in which the effectiveness of lead as measured by the increase in the critical compression ratio accompanying the addition of lead tetraethyl per c.c. of lead per gallon has been plotted against the number of carbon atoms in the molecule for convenience. As is evident, the compounds show a wide range of variation, the compounds in which lead is more effective appearing as those which usually have a double bond removed from the end of the molecule.

A certain amount of data is available on the effect of the location of the unsaturated linkage in straight-chain unsaturated compounds on the effectiveness of lead in the compounds, and this has been portrayed graphically in Fig. 13. In this representation, the effectiveness of lead in the compound has been plotted against the position of the unsaturated linkage for the pentenes and some heptenes and heptynes. The data are quite incomplete for these series, but they suggest that as the double bond is progressively moved towards the centre of the molecule, the effectiveness of lead in the compound increases. The opposite condition would seem to prevail for the acetylene compounds, however, and this relationship appears somewhat similar to that observed for the critical compression ratios of these same hydrocarbons. It is also of interest to note that in the case of the olefines with the double bond next to the terminal carbon atom or in the alpha position, the lower members of the series are compounds in which lead is more effective when the measurements are made with the pure compounds.

Data on compounds containing a benzene ring with hydrocarbon side chains are represented in Fig. 14, plotted in a manner similar to that used in a previous representation. Considering these particular compounds, it appears that those with a saturated side chain are those in which lead is especially effective. The introduction of unsaturation in the side chain reduces this quality of responding to lead. The compounds which contained a triple bond in what might be termed a conjugated position to the benzene ring exhibited a negative lead effect, and the critical compression ratio of hydrocarbon phenylbutadiene appeared unaffected by lead tetraethyl.

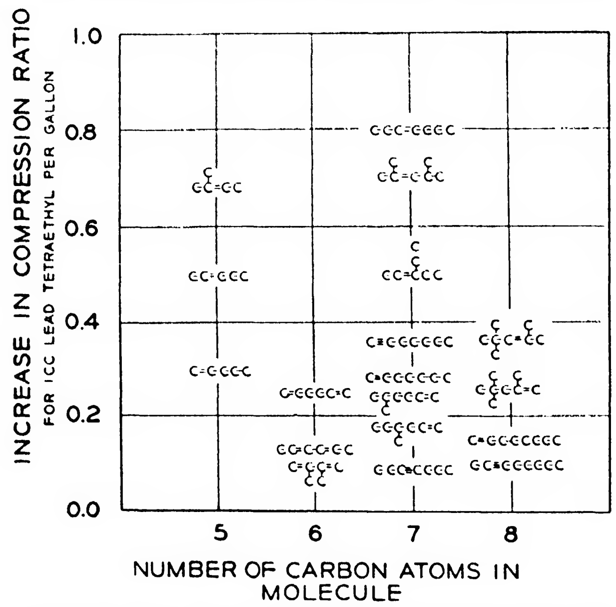


FIG. 12. Effect of structure of unsaturated aliphatic compounds on effectiveness of lead tetraethyl.

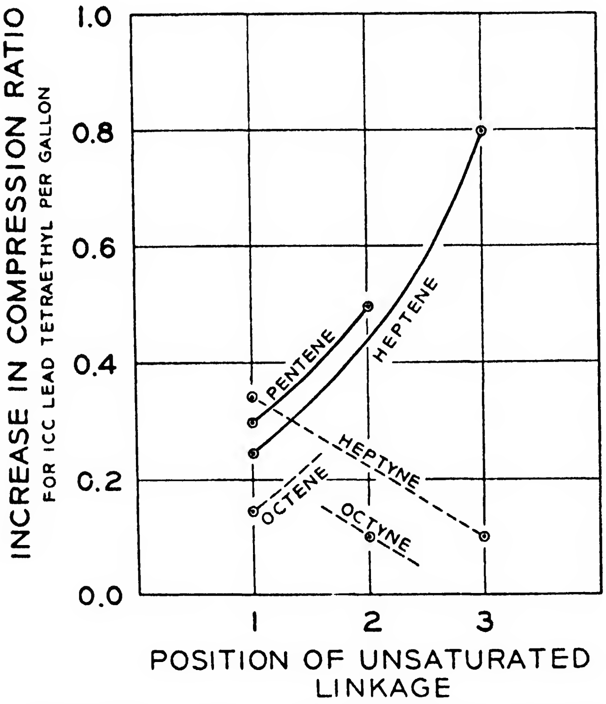


FIG. 13. Effect of position of unsaturation on effectiveness of lead tetraethyl.

Some of the relationships suggested by this representation may be more readily visualized by the diagram of Fig. 15, showing the effect of the successive introduction of double bonds into some cyclic compounds. In the case of the series cyclohexane, cyclohexene, cyclohexadiene the effect of the lead becomes progressively less until in the case

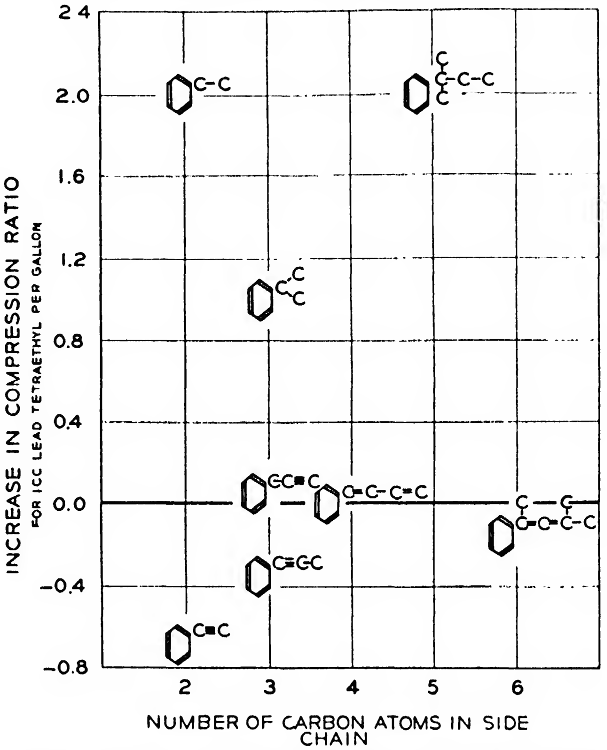


FIG. 14. Effect of side chains of benzene ring on effectiveness of lead tetraethyl.

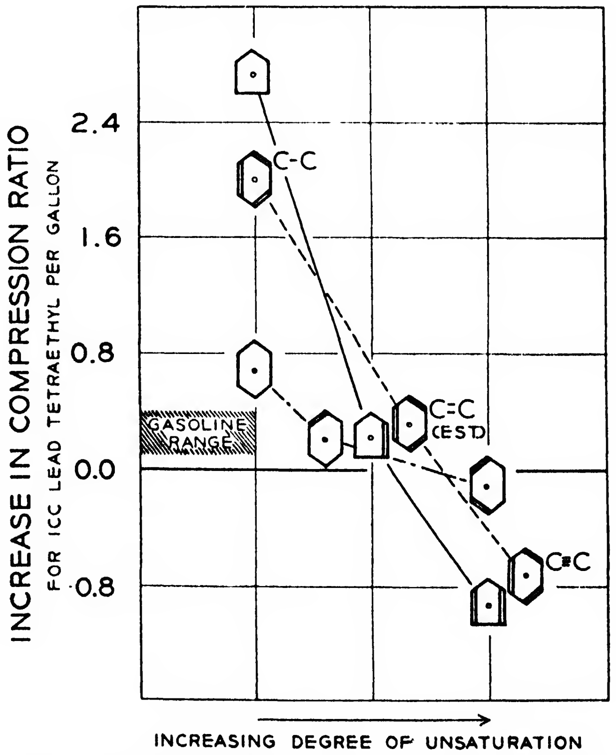


FIG. 15. Effect of double bonds in cyclic hydrocarbons on effectiveness of lead tetraethyl.

of the cyclohexadiene the effect becomes negative. A similar relationship is to be observed in the series cyclopentane, cyclopentene, and cyclopentadiene, although the magnitude of the phenomenon in this case is much greater. The series of ethyl benzene or phenyl ethane, phenyl ethylene, and phenyl acetylene also shows a similar relationship.

APPENDIX

Explanation of Tables

In the following appendix the attempt has been made to gather together the original data on the knocking characteristics of hydrocarbons as well as the effectiveness of lead tetraethyl in them in so far as they are recorded in the literature.

In all cases the values as given for a compound are grouped together for that particular compound. For convenience, the hydrocarbons are arranged in order of increasing molecular weight, and are arranged into tables as follows:

I. Paraffin hydrocarbons.
II. Unsaturated aliphatic hydrocarbons.
III. Aromatic hydrocarbons.
IV. Saturated naphthene hydrocarbons (five-carbon atom ring).
V. Saturated naphthene hydrocarbons (six-carbon atom ring).
VI. Unsaturated naphthene hydrocarbons.
VII. Miscellaneous unsaturated hydrocarbons.

In all cases where it has been possible in addition to the original data the blending octane numbers have also been given, in most cases as computed by Garner, Evans, Sprake, and Broom [13, 1933], since they afford a means of comparing the different values on an approximation to a common basis. In almost all cases, the agreement between different observers is remarkably good, not only in view of the different sources of the hydrocarbons, but more especially in view of the different conditions under which the determinations were made. Such values of blending octane numbers are indicated in parentheses and may be considered as fairly comparable.

The data as originally reported have also been recorded, and the authors, the engine conditions under which the determinations were made, and the units used in expressing the results have been indicated at the tops of the columns containing the numerical data.

The original units in many cases are quite different, and some of them whose significance is less obvious may be defined here:

Aniline Equivalent pertains to dilute solutions of the hydrocarbon. A positive aniline equivalent indicates that the compound knocks less than the reference gasoline to which it has been added and represents the amount of aniline expressed as the number of centigram-mols per litre which must be added to the reference fuel to produce a fuel that is equivalent in tendency to knock to a one-molar solution of the compound in the reference gasoline—that is, to a solution containing one gram.-mol. of the compound made up to a volume of 1,000 c.c. with the reference gasoline. A negative aniline equivalent indicates that the compound knocks more than the reference gasoline and represents the amount of aniline, expressed as centigram-mols per litre, which must be added to the molar solution of the compound in the reference gasoline to make it equivalent in tendency to knock to the reference gasoline.

Blending Octane Number also relates to dilute solutions. It represents the octane number of an ideal fuel (with linear relation between octane number and concentration) which produces an equivalent effect on knock in dilute solution as the compound considered. The value of the blending octane number may be defined more exactly by the equation:

$$O_H = \frac{O_B - O_R}{V} + O_R,$$

where

O_H = blending octane number of hydrocarbon,
O_B = measured octane number of the solution containing V fraction of hydrocarbon by volume,
O_R = measured octane number of reference fuel.

TABLE I

Paraffin Hydrocarbons

	Lovell, Campbell, and Boyd [20]. 600 r.p.m., 212° F. Jacket. 1 g. mol. per litre in 55 octane gasoline. Aniline equivalents. (Blending octane number)†*	*Garner et al. [13]. Series 30 engine, 600 r.p.m. 20% in gasoline. (Blending octane number*)*		*Thornycroft and Ferguson [34]. E-5 engine, 1,500 r.p.m., 140° F. Jacket. 30% in reference fuel. Increase in Compression Ratio. (Blending octane number*)*	*Hoffman et al. [15]. 800 r.p.m., 70° C. Jacket, 40° C. Mixture. 30% in gasoline. Increase in Compression Ratio. (Blending octane number*)*	*Lovell, Campbell, and Boyd [24]. 600 r.p.m., 212° F. Jacket. Critical Compression Ratio*	*Neptune and Trimble [28]. C.F.R. engine. Octane numbers*	*Thornycroft and Ferguson [34]. E-35 engine, 60° C. Jacket. H.U.C.R.*	*Campbell, Signaigo, Lovell, and Boyd [7]. 600 r.p.m., 212° F. Jacket. Increase in Critical Compression Ratio for addition of 1 c.c. lead tetraethyl per gallon.*
		212° F. Jacket	300° F. Jacket						
Methane	..	..	..	..	..	15	..	..	..
Ethane	..	..	..	..	..	14·0	..	..	..
Propane	..	..	..	..	..	12·0	125	..‡	..
n-Butane	..	..	..	..	..	6·4	91§	8·0‡	..
iso-Butane	..	..	..	..	..	8·9	99§	7·5‡	..
n-Pentane	1(60)	(70)	(57·5)	0·4(68)	..	3·8	64§	6·0‡	0·50
2-Methyl butane	9(92)	(94·5)	(82·5)	..	..	5·7	90§	..	0·95
2,2-Dimethyl propane	15(116)	..	..	..	..	..	..	..	..
n-Hexane	[−6(29)] −6(29)	(26·5)	(23·5)	−0·35(39)	−0·28(7)‖	3·3	..	5·0	0·20
2-Methyl pentane	4(69)	..	..	..	−0·04(55)‖	..	..	..	..
3-Methyl pentane	8(84)	..	..	..	..	..	..	..	..
2,2-Dimethyl butane	13(101)	..	..	..	0·57(115)‖	..	..	..	..
2,3-Dimethyl butane	19(124)	..	..	..	0·39(97)‖	..	..	..	..
n-Heptane	[13(14)] 14(0)	(0)	(0)	−1·2(14)	−0·53(−27)	2·8	..	3·7‡¶	0·20
2-Methyl hexane	0(55)	..	..	..	..	..	..	..	..
3-Methyl hexane	3(65)	..	..	..	..	..	..	..	..
2,2-Dimethyl pentane	8(80)	..	..	..	..	..	..	..	..
2,3-Dimethyl pentane	12(94)	..	..	..	..	..	..	..	..
2,4-Dimethyl pentane	8(80)	..	..	..	..	5·0	..	..	0·80
3,3-Dimethyl pentane	13(98)	..	..	..	..	..	..	..	..
2,2,3-Trimethyl butane	19(116)	..	..	..	..	13·0	..	..	..
3-Ethyl pentane	4(68)	..	..	..	..	3·9	..	..	0·20
n-Octane	−21(−19)	(−20)	(−13)	−1·75(−6)	−0·74(−50)	..	..	..	..
2,5-Dimethyl hexane	5(69)	..	..	..	..	..	..	..	..
2,2,4-Trimethyl pentane	[13(93)] 16(100)	(100)	(100)	..	..	7·7	..	..	2·10
2,2,3-Trimethyl pentane	17(105)	..	..	..	..	12·0	..	..	..
2,2,3,3-Tetramethyl butane	26(130)	..	..	..	..	..	..	..	..
n-Nonane	−28(−34)	..	..	..	..	..	..	..	..
2,6-Dimethyl heptane	−6(36)	..	..	..	..	..	..	..	..
n-Decane	−30(−32)	..	..	−2·3 approx.	..	..	..	..	..
2,7-Dimethyl octane	−10(25)	..	..	..	..	3·3	..	..	0·20
3,3,4,4-Tetramethyl hexane	29(124)	..	..	..	..	..	..	..	..
3,4-Diethyl hexane	0(55)**	..	..	..	..	3·9	..	..	..

* Blending octane numbers as computed by Garner, Evans, Sprake, and Broom [13].

† Values in square brackets were determined on C.F.R. engine, 212° F. Jacket, 300° F. Mixture [24].

‡ Ricardo and Thornycroft [30] give values for H.U.C.R. in E-35 engine as follows: propane 8·0, butane 7·65, *n*-pentane 5·7, *n*-heptane 3·75.

§ Alden [1] gives values for octane numbers in C.F.R. engine at 900 r.p.m. as follows: *iso*-butane 100, *n*-butane 92, *iso*-pentane 91, *n*-pentane 64.

‖ Schmidt [31] gives the following values for the compression ratio of a base gasoline to which 10% of paraffin hydrocarbons had been added: *n*-hexane 4·40, 2-methyl pentane 4·61, 2,3-dimethyl butane 4·66, 2,2-dimethyl butane 4·87, *n*-heptane 4·36, *n*-octane 4·25.

¶ Ricardo [29] gives value of 3·75 for H.U.C.R. of *n*-heptane.

** Reference 24.

TABLE II

Unsaturated Aliphatic Hydrocarbons

	Lovell, Campbell, and Boyd [21]. 600 r.p.m.; 212° F. Jacket. 1 g. mol. per litre of 55 octane gasoline. Aniline equivalents. (Blending octane number)†*	*Garner, Wilkinson, and Nash [12]. Series 30 engine, 600 r.p.m. 20% solution in gasoline. Octane number of solution. (Blending octane number*) Values in italics refer to similar data of Garner [10] and blending octane number**		*Nash and Howes [27, 18]. Series 30 engine, 500 r.p.m., 140° F. Jacket. 20% (by volume) solution in gasoline. Equivalent to number of c.c. ethyl fluid per gallon*	*Lovell, Campbell, and Boyd [24]. 600 r.p.m.; 212° F. Jacket. Critical Compression Ratio*	*Neptune and Trimble [28]. Octane numbers in C.F.R. engine.*	*Campbell, Signaigo, Lovell, and Boyd [7]. 600 r.p.m., 212° F. Jacket. Increase in Critical Compression Ratio for addition of 1 c.c. lead tetraethyl per gallon.‡*
		212° F. Jacket	300° F. Jacket				
Ethylene	. .	58·9(85·5)	54·9(82·5)	. .	8·5	. .	. .
Acetylene	. .	. .	. .	. .	4·6	. .	. .
Propylene	. .	61·6(102)	57·2(94·5)	. .	8·4	. .	. .
2-Methyl propene	. .	. .	. .	. .	. .	87	. .
1-Butene	. .	64·4(111·5)	57·4(95)	. .	. .	80	. .
2-Butene	. .	. .	. .	. .	. .	83	. .
1-Pentene	10(98·5)	61·4(98·5)	54·2(82)	. .	5·8	. .	*6·3*‡ 0·30
2-Pentene	[13(107)]† 16(125)	*65·6*(*128*)‡	*60·0*(*112*)‡	3·5	7·0	. .	0·50
2-Methyl-2-butene	[15(122)]† 23(157)	*70*(*150*)‡	*60·5*(*114·5*)‡	4·5	7·0	. .	0·70
1,5-Hexadiene	6(79)	*55·4*(77)‡	. .	. .	4·8	. .	0·25
2,4-Hexadiene	29(174)	. .	. .	. .	6·6	. .	0·10
1-Hexene	0(85)	56·3(80)	52(58·5)	. .	4·6	. .	*7·0*‡
2-Hexene	12(100)	. .	. .	. .	5·4	. .	. .
3-Methyl-2-pentene	14(109)	. .	. .	. .	. .	. .	. .
2,3-Dimethyl-1,3-butadiene	38(212)	. .	. .	. .	8·6	. .	0·10
1-Heptene	0(55)	53·5(59·5)	49·6(54·5)	. .	3·7	. .	*8·1*‡ 0·25
3-Heptene	12(95)	62·7(113·5)	54·8(86)	. .	4·9	. .	0·80
2,3-Dimethyl-2-pentene	21(127)	. .	. .	. .	. .	. .	. .
2,4-Dimethyl-2-pentene	20(122)	. .	. .	. .	8·8	. .	0·70
2,2-Dimethyl-4-pentene	27(147)	. .	. .	. .	10·0	. .	. .
2,2,3-Trimethyl-3-butene	23(132)	. .	. .	. .	12·6	. .	. .
3-Ethyl-2-pentene	20(124)	*57·8*(*133*)‡	*51·5*(*121*)‡	. .	6·6	. .	0·50
1-Heptyne	6(76)§	. .	. .	. .	4·9	. .	0·33
3-Heptyne	. .	. .	. .	. .	3·4	. .	0·10
2-Methyl-5-hexyne	. .	*57·8*(*89*)‡	*51·5*(*69·5*)‡	. .	. .	. .	. .
3-Ethyl-1,3-pentadiene	24(140)	. .	. .	. .	. .	. .	. .
1-Octene	(25)	50(38·5)‡	47(89·5)	. .	3·4	. .	*9·4*‡ 0·15
2-Octene	0(55)	. .	. .	. .	. .	. .	. .
3-Octene	6(73)	. .	. .	. .	. .	. .	. .
4-Octene	12(91)	. .	. .	. .	. .	. .	. .
2-Octyne	2(62)§	. .	. .	. .	4·0	. .	0·10
2-Methyl-5-hexene	8(83)	. .	. .	. .	4·7	. .	0·25
3-Methyl-5-hexene	9(86)	. .	. .	. .	5·0	. .	0·20
2,2,4-Trimethyl-3-pentene	30(144)	. .	. .	6·6	10·0	. .	0·35
2,2,4-Trimethyl-4-pentene	32(150)	. .	. .	. .	11·3	. .	0·25
1-Nonene	. .	44(15)	40(20)	. .	. .	. .	*11·1*‡

* Blending octane numbers computed by Garner, Evans, Sprake, and Broom [13].

† These values were determined on C.F.R. engine, 900 r.p.m., 212° F. Jacket, 300° F. Mixture [24].

‡ These values are data of Garner, Wilkinson, and Nash [12] given in increase in octane number of 20% solutions of the hydrocarbons in gasoline for the addition of 1 c.c. lead tetraethyl per gallon measured in Series 30 engine, 600 r.p.m., 212° F. Jacket.

§ Reference 24.

TABLE III

Aromatic Hydrocarbons

	*Lovell, Campbell, and Boyd [23]. 600 r.p.m., 212° F. Jacket. 1 g. mol. per litre of 55 octane gasoline. Aniline equivalents. (Blending octane number)**	*Garner and Evans [11]. Series 30 engine, 600 r.p.m. 20% solution by volume in gasoline. Octane number of solution. (Blending octane number*)*		*Howes and Nash [18]. Series 30 engine, 500 r.p.m., 140° F. Jacket. 20% solution by volume in gasoline. Equivalent to number of c.c. of ethyl fluid per gallon. (Blending octane number*)*	*Hoffman et al. [16, 17]. 800 r.p.m., 70° F. Jacket. 40° C. Mixture, 30% by volume in gasoline. Increase in Compression Ratio. (Blending octane number*)*	*Lovell, Campbell, and Boyd [24]. 600 r.p.m., 212° F. Jacket. Critical Compression Ratio.*	*Ricardo [29]. H.U.C.R.*	*Campbell, Signaigo, Lovell, and Boyd [7]. 600 r.p.m., 212° F. Jacket. Increase in Critical Compression Ratio for addition of 1 c.c. lead tetraethyl per gallon.*
		212° F. Jacket	300° F. Jacket					
Benzene	[6(87)]† 10(108)	60·2(101)	55·2(88)	2·1(96)§‖¶**	0·49(108)	> 15	6·9	*7·4, 9·2*‡
Toluene	[8(90)]† 15(120)	62·2(113)	58(102)	2·75(106·5)‖¶**	0·72(127)	13·6	> 7·0	*7·8, 11·2*‡
Phenyl acetylene	5(76)	..	..	..	0·14(65)	12·4	..	−0·80
Phenyl ethylene	20(137)	..	..	..	0·54(113)	14·0	..	..
Ethyl benzene	[11(97)]† 19(128)	64·1(120·5)	60(112)	3·8(123)**	0·58(117)	10·5	..	*8·9, 11·8*‡ 2·00
o-Xylene	[11(97)]† 17(121)	..	..	3·2(114·0)	0·93(142)	9·6	..	..
m-Xylene	[13(104)]† 23(144)	..	..	4·0(125·5)	0·93(142)	13·6	..	..
p-Xylene	[13(104)]† 26(154)	..	..	4·2(128)	0·93(142)	14·2	..	..
1-Phenyl propyne	11(97)	..	..	..	..	7·4	..	0·12
3-Phenyl propyne	8(86)	..	..	..	..	11·8	..	−0·30
p-Tolyl ethylene	30(163)	..	..	..	..	..	..	..
n-Propyl benzene	24(137)	64(120)	59·9(112)	..	..	10·1	..	*9·0, 11·9*‡
iso-Propyl benzene	22(128)	..	..	2·6(104·5)	..	11·9	..	..
1,2-Methylethyl benzene	15(107)	..	..	..	..	..	..	..
1,3-Methylethyl benzene	22(130)	..	..	..	..	..	..	..
1,4-Methylethyl benzene	27(147)	..	..	..	..	..	..	..
1,3,5-Trimethyl benzene	[16(109)]† 31(161)	66·2(131)	64·4(134)	..	..	14·8	..	*9·9*‡
1,2,4-Trimethyl benzene	20(123)	..	..	..	..	..	..	..
2-*o*-Tolyl propene	25(134)	..	..	..	..	..	..	..
2-*m*-Tolyl propene	37(173)	..	..	..	..	..	..	..
2-*p*-Tolyl propene	37(173)	..	..	..	..	..	..	..
1-*p*-Tolyl propene	29(148)	..	..	..	..	..	..	..
Tetrahydronaphthalene	19(121)	..	..	..	..	..	..	..
n-Butyl benzene	20(115)	62·1(110·5)	56·8(102·0)	..	..	..	..	*7·3, 9·6*‡
iso-Butyl benzene	20(115)	..	..	..	..	7·7	..	..
sec-Butyl benzene	21(119)	..	..	1·8(91)	..	10·1	..	..
tert-Butyl benzene	25(130)	..	..	3·2(114)	..	12·5	..	..
1,2-Methyl-*n*-propyl benzene	19(114)	..	..	..	..	..	..	..
1,3-Methyl-*n*-propyl benzene	25(130)	..	..	..	..	..	..	..
1,4-Methyl-*n*-propyl benzene	25(130)	..	..	..	..	..	..	..
1,2-Methyl-iso-propyl benzene	20(117)	..	..	..	..	..	..	..
1,3-Methyl-iso-propyl benzene	26(134)	..	..	..	..	..	..	..
1,4-Methyl-iso-propyl benzene	27(136)	..	..	4·2(128)	..	11·1	..	1·00
1,3-Diethyl benzene	[24(126)]† 30(145)	..	..	..	..	10·8	..	..
1,4-Diethyl benzene	34(158)	..	..	..	..	9·3	..	..
1-Phenyl-1,3-butadiene	[30(149)]† 33(158)	..	..	..	..	9·5	..	0·0
n-Amyl benzene	17(101)	..	..	..	..	..	..	..
tert-Amyl benzene	23(118)	..	..	3·2(114)	..	12·1	..	2·0
1,4-Methyl-tert-butyl benzene	..	..	..	3·8(123)	..	..	..	..
1,2-Methyl-*n*-butyl benzene	17(102)	..	..	..	..	..	..	..
1,3-Methyl-*n*-butyl benzene	21(113)	..	..	..	..	..	..	..
1,4-Methyl-*n*-butyl benzene	25(123)	..	..	..	..	..	..	..
Trimethyl phenyl allene	36(154)	..	..	..	..	8·3	..	−0·20
1,2-Methyl-*n*-amyl benzene	14(90)	..	..	..	..	..	..	..
1,3-Methyl-*n*-amyl benzene	14(90)	..	..	..	..	..	..	..
1,4-Methyl-*n*-amyl benzene	18(100)	..	..	..	..	..	..	..

TABLE III—*continued*

	Lovell, Campbell, and Boyd [23]. 600 r.p.m., 212° F. Jacket. 1 g. mol. per litre of 55 octane gasoline. Aniline equivalents. (Blending octane number)*	*Garner and Evans [11]. Series 30 engine, 600 r.p.m. 20% solution by volume is gasoline. Octane number of solution. (Blending octane number*)*		*Howes and Nash [18]. Series 30 engine, 500 r.p.m., 140° F. Jacket. 20% solution by volume in gasoline. Equivalent to number of c.c. of ethyl fluid per gallon. (Blending octane number*)*	*Hoffman et al. [16, 17]. 800 r.p.m., 70° F. Jacket. 40° C. Mixture, 30% by volume in gasoline. Increase in Compression Ratio. (Blending octane number*)*	*Lovell, Campbell, and Boyd [24]. 600 r.p.m., 212° F. Jacket. Critical Compression Ratio.*	*Ricardo [29]. H.U.C.R.*	*Campbell, Signaigo, Lovell, and Boyd [7]. 600 r.p.m., 21° F. Jacket. Increase in Critical Compression Ratio for addition of 1 c.c. lead tetraethyl per gallon.*
1,2-Methyl-iso-amyl benzene	16(95)	..	..	..	..	..	..	..
1,3-Methyl-iso-amyl benzene	20(104)	..	..	..	..	..	..	..
1,4-Methyl-iso-amyl benzene	26(120)	..	..	..	..	..	..	..
Phenyl cyclohexene	26(130)	..	..	..	..	..	..	..
Phenyl cyclohexane	−7(31)	..	..	..	..	..	..	..
Diphenyl methane	26(128)	..	..	..	..	..	..	..
n-Heptyl benzene	−3(46)	..	..	..	..	..	..	..

---

* Blending octane numbers as computed by Garner, Evans, Sprake, and Broom [13].

† These values were determined on C.F.R. engine, 900 r.p.m., 212° F. Jacket, 300° F. Mixture [24].

‡ These values are data of Garner and Evans [11] given in increase in octane number of 20% solutions of the hydrocarbons in gasoline for the addition of 1 c.c. lead tetraethyl per gallon measured in Series 30 engine, 600 r.p.m., 212° F. and 300° F. Jacket respectively.

§ Birch and Stansfield [2] found for 20% by weight in gasoline in E-5 engine a change in H.U.C.R. of 0·27; the mixture was equivalent to 61·2% benzene in *n*-heptane (value of base fuel 55·3). (Blending octane number* of 105.)

‖ Garner et al. [12] give values for blending octane numbers of 101 and 118 respectively for benzene and toluene as computed from data of Thornycroft and Ferguson [34].

¶ Schmidt [31] gives values of the compression ratio of a base gasoline to which 10% of benzene and toluene have been added of 4·61 4·93 respectively.

** Blending octane numbers as computed by Garner and Evans [11].

TABLE IV

Saturated Naphthene Hydrocarbons (Five Carbon Atom Ring)

	Lovell, Campbell, and Boyd [23]. *600 r.p.m., 212° F. Jacket. 1 g. mol. per litre of 55 octane gasoline. Aniline equivalents. (Blending octane number*)*†	*Garner and Evans* [11]. *Series 30 engine, 600 r.p.m. 20% by volume in gasoline. Octane number of solution. (Blending octane number*)*		*Hoffman et al.* [15, 17]. *800 r.p.m., 70° C. Jacket, 40° C. air. 30% by volume in gasoline. Increase in Compression Ratio. (Blending octane number*)*	*Lovell, Campbell, and Boyd* [24]. *600 r.p.m., 212° F. Jacket. Critical Compression Ratio.*	*Garner and Evans* [11]. *Increase in octane number of 20% solution in gasoline for 1 c.c. tetraethyl lead per gallon. Series 30 engine, 212° F. and 300° C. Jacket respectively.*
		212° F. Jacket	300° F. Jacket			
Cyclopentane	[12(116)] 14(125)	64·2(122)	60·4(114)	0·26(82)	10·8	8·2‡
Methyl cyclopentane	4(71)	57·8(89·0)	54(84)	0·18(72)	..	8·7
1,3-Dimethyl cyclopentane	−1(51)	57(85)	55(87)	..	4·2	9·4, 9·9
Ethyl cyclopentane	1(59)	51·3(57)	49·5(57)	..	3·9	9·9
1,3-Methylethyl cyclopentane	−3(44)	..	..	..	3·6	..
n-Propyl cyclopentane	−10(16)	45(27)	−(32)	..	..	11·2
1,3-Methyl-*n*-propyl cyclopentane	−7(31)	..	..	..	..	..
n-Butyl cyclopentane	−19(−11)	40(0)	39·5(9·5)	..	..	12·6
1,3-Methyl-*n*-butyl cyclopentane	−19(−4)	..	..	..	..	..
n-Amyl cyclopentane	−23(−19)	..	..	..	2·8	..
1,3-Methyl-*n*-amyl cyclopentane	−22(−9)	..	..	..	..	..
1,3-Methyl-iso-amyl cyclopentane	−19(0)	..	..	..	..	..

* Blending octane numbers as computed by Garner, Evans, Sprake, and Broom [13].

† Values in brackets were determined on C.F.R. engine, 900 r.p.m., 212° F. Jacket, 300° F. Mixture [24].

‡ Campbell, Lovell, Signaigo, and Boyd (7) give 2·7 comp. ratio increase for 1 c.c. tetraethyl lead per gallon.

TABLE V

Saturated Naphthene Hydrocarbons (Six Carbon Atom Ring)

	Lovell, Campbell, and Boyd [22]. 600 r.p.m., 212° F. Jacket. 1 g. mol. per litre of 55 octane gasoline. Aniline equivalents. (Blending octane number)†*	*Garner and Evans [11]. Series 30, 600 r.p.m. 20% by volume in gasoline. Octane number of solution. (Blending octane number*)*		*Hoffman et al. [16, 17]. 800 r.p.m., 70° C. Jacket, 40° C. air. 30% by volume in gasoline. Increase in Compression Ratio. (Blending octane number*)*	*Lovell, Campbell, and Boyd [24]. 600 r.p.m., 212° F. Jacket. Critical Compression Ratio.*	*Thornycroft and Ferguson [34]. E-35 engine. H.U.C.R.*	*Campbell, Signaigo, Lovell, and Boyd [7]. 600 r.p.m., 212° F. Jacket. Increase in Critical Compression Ratio for addition of 1 c.c. lead tetraethyl per gallon.‡*
		212° F. Jacket	300° F. Jacket				
Cyclohexane	[6(81)]† 7(86)	59·1(97·5)	53·8(84)	0·12(63)	4·5§‖¶**	>6	*6·5, 10·5‡* 0·65
Methyl cyclohexane	[5(81)]† 5(74)	55·7(75)	51·5(65·5)	0·34(90)	4·6	6	*9·5‡* 0·30
1,2-Dimethyl cyclohexane	[2(62)]† 6(75)	56·2(81)	51·8(71·0)	0·49(108)	5·1	..	*8·4‡* 0·35
1,3-Dimethyl cyclohexane	4(68)	53·7(68·5)	51·5(69·5)	..	4·4	..	*9·8‡* 0·21
1,4-Dimethyl cyclohexane	6(75)	54·7(73·5)	50·1(62·5)	0·49(108)	4·3	..	*8·3, 11·0‡*
1,3,5-Trimethyl cyclohexane	2(61)	..	..	..	..	..	..
Ethyl cyclohexane	−3(44)	48(41)	44(35·5)	0·21(75)	3·8	..	*9·1, 10·8‡*
Cyclohexyl acetylene	9(88)††	..	..	..	4·6	..	0·21
1,2-Methyl ethyl cyclohexane	[0(55)]† 0(55)	..	..	..	4·3	..	0·16
1,3-Methyl ethyl cyclohexane	−6(34)	..	..	..	3·8	..	0·12
1,4-Methyl ethyl cyclohexane	−8(27)	..	..	..	3·7	..	0·13
1,3-Diethyl cyclohexane	−13(13)	..	..	..	3·2	..	..
1,4-Diethyl cyclohexane	−13(13)	..	..	..	3·3	..	..
n-Propyl cyclohexane	−10(20)	42·7(14·0)	41(15)	..	..	..	*11·4‡*
iso-Propyl cyclohexane	0(55)	..	..	..	..	..	..
1,2-Methyl-*n*-propyl cyclohexane	[−6(71)]† −5(37)	..	..	..	3·6	..	0·12
1,3-Methyl-*n*-propyl cyclohexane	−10(22)	..	..	..	3·4	..	0·12
1,4-Methyl-*n*-propyl cyclohexane	−10(20)	..	..	..	3·3	..	0·12
1,4-Methyl-iso-propyl cyclohexane	1(58)	..	..	..	4·0	..	0·26
n-Butyl cyclohexane	−16(3)	39(−5)	37·2(−2)	..	3·3	..	*11·5‡*
iso-Butyl cyclohexane	−6(35)	..	..	..	..	..	..
sec-Butyl cyclohexane	−3(45)	..	..	..	3·6	..	..
tert-Butyl cyclohexane	16(99)	..	..	..	..	..	..
1,2-Methyl-*n*-butyl cyclohexane	[−13(87)]† −16(6)	..	..	..	3·4	..	0·10
1,3-Methyl-*n*-butyl cyclohexane	−20(−5)	..	..	..	3·3	..	0·10
1,4-Methyl-*n*-butyl cyclohexane	−20(−5)	..	..	..	3·2	..	0·10
1,3-Methyl-iso-butyl cyclohexane	−5(41)	..	..	..	..	..	..
n-Amyl cyclohexane	−21(−8)	..	..	..	3·1	..	..
iso-Amyl cyclohexane	−14(14)	..	..	..	3·3	..	..
tert-Amyl cyclohexane	6(70)	..	..	..	4·2	..	..
1,2-Methyl-*n*-amyl cyclohexane	−17(8)	..	..	..	3·2	..	0·10
Deca-hydronaphthalene	−3(44)	..	..	..	3·6	..	0·13
Dicyclohexane	−21(−8)	..	..	..	..	..	..
Cycloheptane	−6(27)	..	..	..	..	..	..

* Blending octane numbers as computed by Garner, Evans, Sprake, and Broom [13].

† These values were determined on C.F.R. engine, 900 r.p.m., 212° F. Jacket, 300° F. Mixture.

‡ These figures are data of Garner and Evans [11] given in increase in octane number of 20% solutions in gasoline for the addition of 1 c.c. lead tetraethyl per gallon measured in Series 30 engine, 600 r.p.m., 212° F. and 300° F. Jacket respectively.

§ Schmidt [31] gives a value of 4·51 for the compression ratio of a base gasoline to which 10% of cyclohexane had been added.

‖ Birch and Stansfield [2] found for 20% by weight in gasoline in an E-5 engine a change in H.U.C.R. of 0·26; the mixture was equivalent to 61·0% benzene in *n*-heptane (value of base fuel 55·3). (Blending octane number* of 101.)

¶ Blending octane number* of 90 from data of Thornycroft and Ferguson [34].

** Howes and Nash [19] in a Series 30 engine, 500 r.p.m., found a 20% solution by volume in gasoline to be equivalent to 1 c.c. of ethyl fluid per gallon.

†† Reference 24.

Table VI

Unsaturated Naphthene Hydrocarbons

	Lovell, Campbell, and Boyd [22]. 600 r.p.m., 212° F. Jacket. 1 g. mol. per litre of 55 octane gasoline. Aniline equivalents. (Blending octane number)†*	*Hoffman et al. [16, 17]. 800 r.p.m., 70° C. Jacket, 40° C. air. 30% by volume in gasoline. Increase in Compression Ratio. (Blending octane number*)*	*Lovell, Campbell, and Boyd [24]. 600 r.p.m., 212° F. Jacket. Critical Compression Ratio.*	*Campbell, Signaigo, Lovell, and Boyd [7]. 600 r.p.m., 212° F. Jacket. Increase in Critical Compression Ratio for addition of 1 c.c. lead tetraethyl per gallon.*
Cyclopentene	[14(118)] 16(140)	0·36(92)	7·9	0·20
1-Methyl cyclopentene	20(143)	0·48(108)	..	..
1-Ethyl cyclopentene	12(102)	..	..	..
1-*n*-Propyl cyclopentene	12(96)	..	.	..
1-*n*-Butyl cyclopentene	9(82)	..	..	..
1-*n*-Amyl cyclopentene	3(63)	..	..	..
Cyclohexene	[9(97)] 10(102)	0·62(120)‡§‖	4·8	0·20
1-Methyl cyclohexene	20(133)	‡	4·8	..
1,2-Dimethyl cyclohexene	19(121)	..	..	..
2,4-Dimethyl cyclohexene	19(120)	..	..	..
1-Ethyl cyclohexene	13(100)	..	..	..
1-Methyl-2-ethyl cyclohexene	25(133)	..	..	..
2-Ethyl-4-methyl cyclohexene	20(117)	..	..	..
1-Ethyl-4-methyl hexene	18(110)	..	..	..
1-Methyl-2-*n*-propyl cyclohexene	18(105)	..	..	..
1-*n*-Propyl-4-methyl cyclohexene	12(88)	..	..	..
2-*n*-Propyl-4-methyl cyclohexene	18(105)	..	..	..
1-*n*-Butyl cyclohexene	3(63)	..	..	..
1-Methyl-2-*n*-butyl cyclohexene	13(88)	..	..	..
1-*n*-Butyl-4-methyl cyclohexene	7(73)	..	..	..
2-*n*-Butyl-4-methyl cyclohexene	13(88)	..	..	..
1-*n*-Amyl cyclohexene	1(58)	..	..	..
1-*iso*-Amyl cyclohexene	−3(45)	..	..	..
1-Methyl-2-*n*-amyl cyclohexene	11(81)	..	..	..
1-Cyclohexyl cyclohexene	5(69)	..	..	..

* Blending octane numbers as computed by Garner, Evans, Sprake, and Broom [13].

† Values in brackets were determined on C.F.R. engine, 900 r.p.m., 212° F. Jacket, 300° F. Mixture [24].

‡ Birch and Stansfield [2] found for a 20% by weight solution in gasoline in an E-5 engine a change in H.U.C.R. of 0·65 and 0·72 for cyclohexene and methyl cyclohexene respectively. (Blending octane numbers of 129 and 155.) The mixtures were equivalent to 68·3% and 65·1% respectively of benzene in *n*-heptane, and a similar value of the base fuel was 55·3.

§ Howes and Nash [19] found 20% cyclohexene in gasoline to be equivalent to 2·4 c.c. ethyl fluid in the gasoline. (Blending octane number* 99.)

‖ Blending octane number* of 125 as computed from data of Thornycroft and Ferguson [34].

TABLE VII

Miscellaneous Unsaturated Hydrocarbons

	Lovell, Campbell, and Boyd [23]. 600 r.p.m., 212° F. Jacket. 1 g. mol. per litre in 55 octane gasoline. Aniline equivalents. (Blending octane number)†	*Hoffman et al. [16, 17]. 800 r.p.m., 70° C. Jacket. 40° C. Mixture, 30% in gasoline. Increase in Compression Ratio. (Blending octane number*)*	*Lovell, Campbell, and Boyd [24]. 600 r.p.m., 212° F. Jacket. Critical Compression Ratio.*	*Campbell, Signaigo, Lovell, and Boyd [7]. 600 r.p.m., 212° F. Jacket. Increase in Critical Compression Ratio for addition of 1 c.c. lead tetraethyl per gallon.*
Cyclopentadiene . . .	34(250)	0·76(132)	10·9	−0·90
Dicyclopentadiene . . .	65(283)	1·18(153)	11·0	−0·30
1,3-Cyclohexadiene . . .	97(244)	. .	5·9	−0·02
1,4-Cyclohexadiene . . .	95(198)	. .	. .	. .
Diemthyl fulvene . . .	61(295)	. .	9·2	−0·13
Methylphenyl fulvene . .	36(157)	. .	. .	. .
Indene	[16(120)] 21(140)	. .	11·2	−0·10

* Blending octane numbers as computed by Garner, Evans, Sprake, and Broom [13].

† Value in brackets was determined on C.F.R. engine, 900 r.p.m., 212° F. Jacket, 300° F. Mixture (24).

REFERENCES

1. ALDEN, R. C. *Nat. Petr. News*, **24**, no. 3, 32 (1932).
2. BIRCH, S. F., and STANSFIELD, R. *Nature*, **123**, 490 (1929).
3. ——— *Nature*, **123**, 639 (1929).
4. CAMPBELL, J. M., LOVELL, W. G., and BOYD, T. A. *J.S.A.E.* **29**, 129 (1931).
5. ——— *Ind. Eng. Chem.* **10**, 20 (1928).
6. ——— *J.S.A.E.* **26**, 163 (1930).
7. CAMPBELL, J. M., SIGNAIGO, F. K., LOVELL, W. G., and BOYD, T. A. *Ind. Eng. Chem.* **27**, 593 (1935).
8. EDGAR, G. *Ind. Eng. Chem.* **19**, 145 (1927).
9. EGLOFF, G., and MORRELL, J. C. *Ind. Eng. Chem.* **18**, 354 (1926).
10. GARNER, F. H. *Inst. Auto. Eng.*, **27**, 586 (1932).
11. GARNER, F. H., and EVANS, E. B. *J.I.P.T.* **18**, 751 (1932).
12. GARNER, F. H., WILKINSON, R., and NASH, A. W. *J.S.C.I.* **51**, 265 T (1932).
13. GARNER, F. H., EVANS, E. B., SPRAKE, C. H., and BROOM, W. E. S. *Proc. World Petr. Congress*, vol. ii, 170 (1933).
14. HEBL, L. E., and RENDEL, T. B. *J.I.P.T.* **18**, 187 (1932).
15. HEBL, L. E., RENDEL, T. B., and GARTON, F. L. *Ind. Eng. Chem.* **25**, 187 (1933).
16. HOFFMAN, F., LANG, K. F., BERLIN, K., and SCHMIDT, A. W. *Brenn. Chem.* **14**, 103 (1933).
17. ——— *Brenn. Chem.* **14**, 103 (1933).
18. HOWES, D. A., and NASH, A. W. *J.S.C.I.* **49**, 16 T (1930).
19. HOWES, D. A., and NASH, A. W. *J.S.C.I.* **49**, 113 T (1930).
20. LOVELL, W. G., CAMPBELL, J. M., and BOYD, T. A. *Ind. Eng. Chem.* **23**, 26 (1931).
21. ——— *Ind. Eng. Chem.* **23**, 555 (1931).
22. ——— *Ind. Eng. Chem.* **25**, 1107 (1933).
23. ——— *Ind. Eng. Chem.* **26**, 475 (1934).
24. ——— *Ind. Eng. Chem.* **26**, 1105 (1934).
25. MIDGLEY, T., JR. *J.S.A.E.* **7**, 489 (1920).
26. MIDGLEY, T., JR., and BOYD, T. A., *Ind. Eng. Chem.* **14**, 589 (1922).
27. NASH, A. W., and HOWES, D. A. *Nature*, **123**, 276 (1929).
28. NEPTUNE, F. B., and TRIMBLE, H. M. *Oil and Gas J.* **32**, no. 51, 44 (1932).
29. RICARDO, H. R. *Auto. Eng.* 1921, **11**, 51, 92 (1921).
30. RICARDO, H. R., and THORNYCROFT, D. *Trans. World Power Conference*, **3**, 674 (1928).
31. SCHMIDT, A. W. *Petr. Z.* **28**, Mar. 9 Motorenbetrieb, p. 2 (1932).
32. —— *Z. Angew Chem.* **44**, 476 (1931).
33. STEVENS, D. R., and MARLEY, S. P. *Ind. Eng. Chem.* **19**, 228 (1927).
34. THORNYCROFT, O., and FERGUSON, A. *J.I.P.T.* **18**, 329 (1932).
35. VEAL, C. B., BEST, H. W., CAMPBELL, J. M., and HOLADAY, W. M. *J. Soc. Auto. Eng.* **32**, 105 (1933).

11. ANTI-KNOCK COMPOUNDS

By GEORGE CALINGAERT, D.Sc.

Research Laboratories of the Ethyl Gasoline Corporation, Detroit, Mich.

Introduction

THE term 'anti-knock compound' or, simply, 'anti-knock' refers to a number of materials which have the property, when added in small amounts to the fuel charge of an internal-combustion engine, of suppressing or at least of strongly decreasing knocking. The term has been sometimes loosely applied to cover also undoped fuels which have little or no tendency to knock. Present practice, however, reserves the name 'anti-knock' for addition agents (or 'dopes'), and uses the name 'non-knocking fuels' to cover both the fuels which pre-ignite before they knock (benzene, ethyl alcohol, &c.), and those whose tendency to knock is so slight that they never reach the knocking-point under ordinary conditions ('iso-octane', &c.).

The discovery of the existence of anti-knock compounds, as well as the discovery of most of the members of the group, is to be credited to Midgley and Boyd working under the guidance and at the inspiration of C. F. Kettering [5, 1924; 24, 1920; 25, 1923]. Since the time of these original publications, the list of anti-knock compounds or classes of compounds has not been lengthened significantly. Boyd [5, 1924] has extended the list of the known anti-knock compounds of nitrogen, Egerton [8, 1930] has discussed the effect of thallium, and Müller-Cunradi [26, 1930] that of iron carbonyl.

The present chapter gives a general idea of the compounds which are known to have anti-knock properties and discusses their relative effectiveness. The anti-knock compounds which have at times been considered to have commercial value are discussed in greater detail, and methods are given for the detection and quantitative determination of these compounds in gasoline. The very interesting problem of the mechanism of anti-knock action is intimately related to the theory of knock itself, and is, therefore, included in other articles of this section, e.g. 1 and 2.

Relative Anti-knock Value of Different Compounds

The evaluation of anti-knock effect necessitates measurements of the little-understood phenomenon called 'engine knock'. The discussion in Article 15 of this complex phenomenon makes it clear that the occurrence and intensity of knock is profoundly affected by a large number of variables, of which the fuel composition (with or without anti-knock compounds) is only one. This means that any relative rating given for two or more anti-knock compounds holds only under the particular conditions of test. Fortunately, the various experimenters have always aimed to maintain reasonably normal operating conditions, so that in most cases their results are fairly representative of automobile engine performance, although variations in relative anti-knock effectiveness up to 30 or even 50% may still be observed when the conditions of the tests are changed. The two major exceptions are the aromatic type of non-knocking fuels and the metal carbonyl anti-knock compounds, which, when compared with aniline or lead tetraethyl, for instance, may vary several-fold in anti-knock effectiveness when the engine operating conditions are changed over comparatively short ranges, all well within those occurring in practice. These special cases will be illustrated later, and their occurrence should not materially affect the comparison of anti-knock compounds in general.

A representative list of anti-knock compounds is given in Table I. The anti-knock effectiveness is expressed as the reciprocal of the number of mols. giving the same effect as 1 mol of aniline, so that the numbers are a direct measure of anti-knock effectiveness. The data given by different authors have all been recalculated to the same basis. They are, however, listed separately, because even slight variations in testing methods may affect the results, so that data from different sources are seldom strictly comparable.

TABLE I

Relative Effectiveness of Anti-knock Compounds

(Reciprocal of number of mols giving the same anti-knock effect as 1 mol of aniline.)

A. *Data of Campbell, Lovell, and Boyd* [14, 1930], *and of Midgley and Boyd* [5, 1924; 25, 1922–3]

Benzene*	0·085
2, 2, 4-Trimethylpentane*	0·085
Ethyl alcohol*	0·104
Xylene*	0·142
Aniline	1·000
Ethyl iodide	1·09
Titanium tetrachloride	3·2
Tin tetraethyl	4·0
Diethyl selenide	6·9
Diethyl telluride	26·6
Nickel carbonyl	35
Iron carbonyl†	50
Lead tetraethyl	118

* Non-knocking fuels, listed here for the purpose of comparison.
† Data from the authors' laboratory.

B. *Data of Charch, Mack, and Boord* [6, 1926]

[Aniline	1·0]
Cadmium dimethyl	1·24
Triphenylarsine	1·6
Titanium tetrachloride	3·2
Stannic chloride	4·1
Bismuth triethyl	23·8
Lead tetraethyl	118

In addition to the data reported above, Egerton also stated that thallium compounds and thallium vapours exerted a pronounced anti-knock effect [8, 1930].

The compounds listed in Table I belong to several groups: metal compounds (halides, organo-metallic compounds), amines, hydrocarbons, &c. A better understanding of the relative values of these anti-knock compounds will be gained by a more extensive study of each group separately.

Non-knocking Fuels. The compounds of the first group are the non-knocking fuels, and most of them exercise an effect which is less than one-tenth of that of a good amino anti-knock compound such as aniline. The amounts of these materials which are normally used (10 to 60%) are sufficient to change the composition of the fuel quite appreciably. In the absence of an absolute scale of measurement of anti-knock action, it is difficult to decide whether the effect obtained is merely the sum of the partial effects of the two fuels or whether the non-knocking fuel also acts as an inhibitor of the knock caused by the other fuel with which it is mixed. There are, however, a few indications that some non-knocking fuels also exert a slight anti-knock effect. As shown in Articles 1 and 2, slow oxidation of the fuel charge prior to ignition is an important factor in knocking. Gill, Mardles, and Tett [11, 1928] have shown that under certain conditions benzene inhibits the slow oxidation of *n*-hexane and cyclohexane, and Beatty and Edgar [3, 1934] have found a similar effect of 2, 2, 4-trimethylpentane on the rate of oxidation of *n*-heptane, thus suggesting that these two hydrocarbons actually affect the tendency to knock of the other hydrocarbons present in the fuel charge.

Amino Compounds. The second group of anti-knock compounds comprises the amino anti-knock compounds. Table II gives the relative effectiveness of a comprehensive series of compounds of this group.

TABLE II

A. *Influence of some Groups attached to the Atom on the Anti-knock Effect of Nitrogen* [5, 1924]

(Reciprocal of number of mols. giving the same anti-knock effect as 1 mol. of aniline.)

Ammonia	−0·09 (pro-knock effect)
Ethylamine	0·20
Diethylamine	0·495
Triethylamine	0·14
Diethylphenylamine	0·24
Ethyldiphenylamine	0·58
Triphenylamine	0·09
Diphenylamine	1·5
Phenylamine (aniline)	1·0

B. *Influence on the Anti-knock Effect of Aniline of Substituting Various Organic Radicals for Hydrogen in the Ring and in the Amino Group* [5, 1924]

Aniline	1·0
Toluidine	1·22
m-Xylidine	1·4
Cumidine	1·51
Ethylaminobenzene	1·14
n-Propylaminobenzene	1·10
n-Butylaminobenzene	1·11
Amylaminobenzene	1·15
Aminobiphenyl	1·14
Monomethylaniline	1·4
Monoethylaniline	1·02
Mono-*n*-propylaniline	0·75
Mono-*n*-butylaniline	0·52
Mono-isoamylaniline	0·248
Diphenylamine	1·5
Dimethylaniline	0·21
Diethylaniline	0·24
Di-*n*-propylaniline	0·27

The anti-knock compounds which contain nitrogen stand out as a special class. They must be considered as true anti-knock compounds, since the most effective have a measurable action at a concentration as low as 0·1%, an amount which can hardly be considered to modify the bulk composition of the fuel. A first point, which is not completely illustrated by Table II, is that the anti-knock effect is not due exclusively to the presence of the element nitrogen, since some nitrogen compounds (nitro compounds, nitrites, &c.) actually cause detonation. The second point, which is well illustrated here, is that the anti-knock effectiveness varies about tenfold, depending on the type of compound used. This effectiveness apparently depends upon a special type of linkage between the nitrogen and the organic radicals. Thus the least effective compounds are those containing no aromatic linkage to the nitrogen, while the most effective contain at least one such linkage and at least one N–H linkage. This is probably related to some oxidation or oxidation-reduction process to which compounds of this type are particularly susceptible. This relation is illustrated in Fig. 1, which is taken from Boyd's publication [5, 1924].

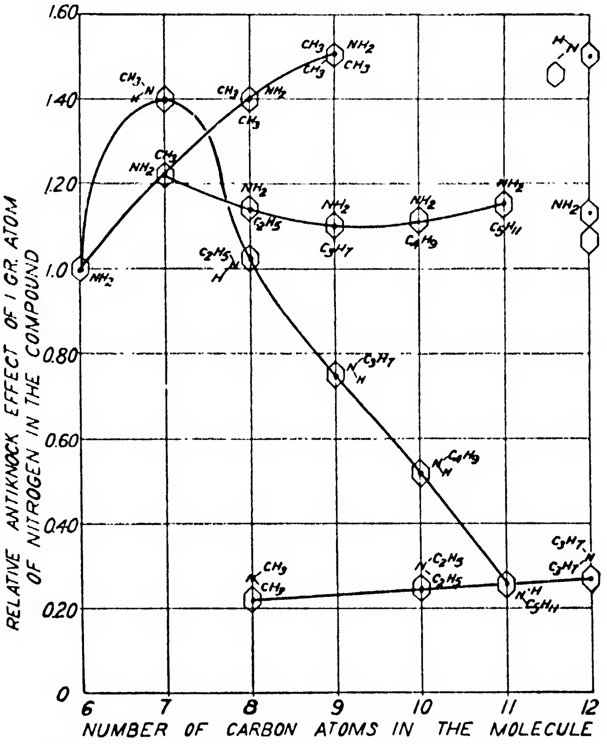


FIG. 1. Influence on the anti-knock effect of aniline of substituting various organic radicals for hydrogen in the ring and in the amino group.

Metallic and other Compounds. The next class comprises compounds of metallic or non-metallic elements, in which the anti-knock action is identified more closely with the element itself. This class, from iodine compounds to lead compounds, covers a 100-fold variation in effectiveness, and contains the most effective anti-knock compounds known.

Table III illustrates the effect of different groups attached to some typical anti-knock elements.

TABLE III

Relative Anti-knock Effectiveness of Different Compounds of the Same Elements

(Reciprocal of number of mols. giving the same anti-knock effect as 1 mol. of aniline.)

A. *Data of Midgley and Boyd* [5, 1924; 25, 1922–3]

Element	*Ethyl compound*	*Phenyl compound*
Iodine	1·09	0·88
Selenium	6·9	5·2
Tellurium	26·8	22·0

B. *Data of Charch, Mack, and Boord* [6, 1929]

Compound	*Anti-knock coefficient*
Lead tetraethyl	118
Lead tetraphenyl	70
Lead diethyl dichloride	79
Lead diphenyldimethyl	115
Lead diphenyldiethyl	109
Lead diphenyl dichloride	85
Lead diphenyl dibromide	71
Lead diphenyl di-iodide	94
Lead tri-*p*-xylyl	77
Lead ethyl xanthogenate	8·3
Lead thioacetate	10·0
Bismuth triphenyl	21·4
Bismuth trimethyl	23·8
Bismuth triethyl	23·8
Stannic chloride	4·1
Stannic iodide	15·1
Tin diethyl di-iodide	14·5
Cadmium dimethyl	1·24
Titanium tetrachloride	3·2
Monophenyl arsine	1·6
Triphenyl arsine	1·6

C. *Data of Gilman and Balassa* [12, 1929]

Lead dibutyldiphenyl	39
Lead di-*iso*butyldiphenyl	45
Lead di-*sec*-butyldiphenyl	53
Lead tetraethyl	118

It is clear that we are dealing here primarily with a property of the element and not of the compound: the change from the ethyl to the phenyl compound causes at most only a 20% change in effectiveness instead of the threefold variation observed between diethyl- and diphenyl-amines. Furthermore, in the case of iodine [16, 1927], and of vapours or fogs of lead, iron, tin, thallium, &c. [4, 1920; 8, 1926], it was shown that the elements themselves have anti-knock effect. The effectiveness in this case depends on the position of the element in the periodic table [21, 1926]. In any case, the element or its compound should be present in the combustion chamber in a highly dispersed form. This may be accomplished by volatilization of the metal in an arc, for instance [4, 1920; 8, 1926], or by introduction in the form of a compound which is soluble in the fuel and volatile [21, 1926].

The Effect of Test Conditions on Anti-knock Value

The broad problem of determining the exact conditions under which to make measurements of knock is treated in Article 15. The present study is concerned only with the effect of variations in condition on the relative ratings of various anti-knock compounds.

A complete study of this problem, including most of the known anti-knock compounds, and covering all the significant variations in operating conditions, is not available, and would perhaps be of little practical value. The information on hand covers primarily those fuels and anti-knock compounds which have been tested most exhaustively, namely, benzene, lead tetraethyl, and iron carbonyl.

Fig. 2 illustrates the effect of a single variable, jacket water temperature, on the relative effectiveness of benzene and lead tetraethyl. Thus, with this particular engine and gasoline, a rise in jacket water temperature from 216 to 350° F. changed the benzene equivalent of 5 c.c. $PbEt_4$/U.S. gal. from 50 to 70%. The magnitude of this effect may change with the fuel used and with the type of engine. The effect is, however, general, and accounts at least partly for the preference given to lead-treated fuels over benzene blends for high-output engines.

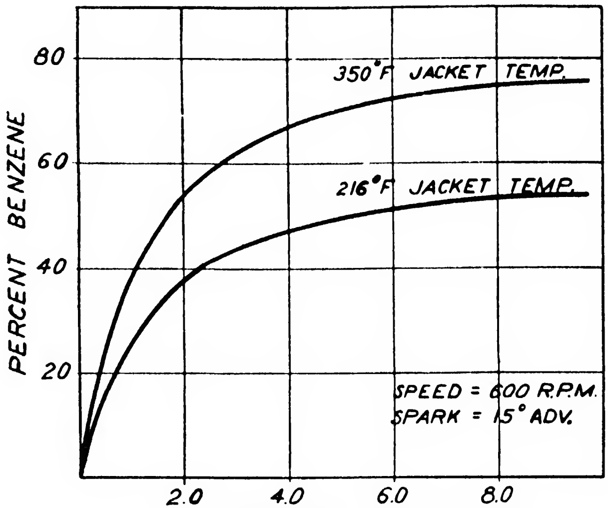


Fig. 2. Lead tetraethyl-benzene equivalent in aviation gasoline.

Fig. 3 illustrates the effect of a change in air-fuel ratio on the relative anti-knock effectiveness of lead tetraethyl and iron carbonyl. In both sets of data plotted here the relative effectiveness of the two compounds varies almost threefold over the range of 11 : 1 to 15 : 1 air-fuel ratio. The two curves, however, are not very different, showing that air-fuel ratio is the most significant variable.

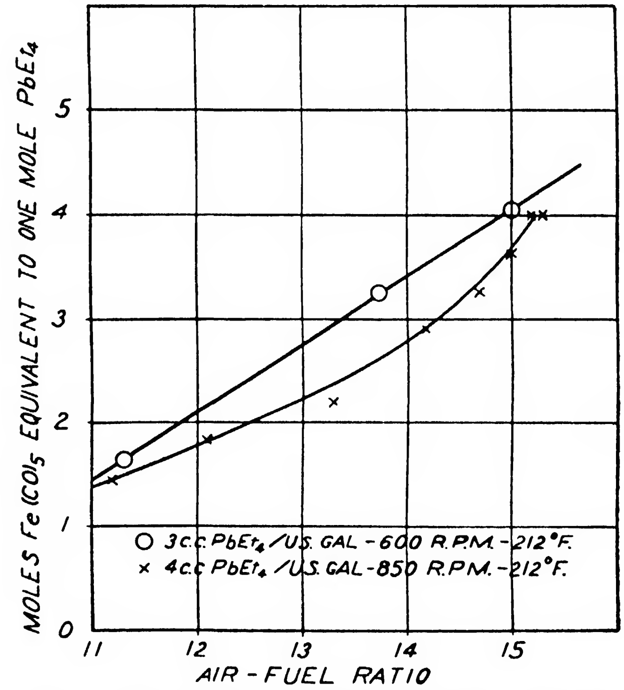


Fig. 3. Effect of mixture ratio upon the relative anti-knock effectiveness of iron carbonyl and lead tetraethyl.

The response of a fuel to the addition of lead tetraethyl (usually referred to as *lead susceptibility*) varies greatly from one fuel to another and even for the same fuel when the test conditions are changed. The first point has been illustrated in the case of pure hydrocarbons by Lovell, Campbell, and Boyd [20, 1935] and is discussed in Article 10. The same holds true in the case of commercial fuels, as illustrated by the data given in Table IV and taken from Hebl, Rendel, and Garton [13, 1932–3] (cf. Article 12).

TABLE IV

Effect of 1 c.c. $PbEt_4$/U.S. Gallon on Various Gasolines

Gasoline	*Octane number*		*Increase in O.N.*
	No Pb	*1 c.c. Pb*	
Stabilized natural	69·4	79·6	10·2
Cracked	70·0	75·5	5·5
50-50 cracked—straight run (West Texas)	62·5	70·0	7·5
West Texas straight run	54·2	61·9	7·7
Mid-Continent „ „	42·5	58·0	15·5

A fair amount of additional data is available in the literature [2, 1932; 13, 1932–3; 27, 1932].

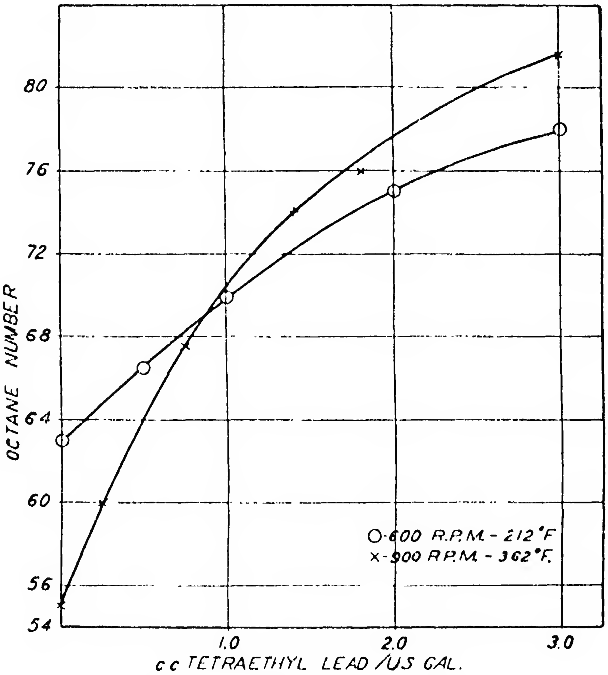


FIG. 4. Lead susceptibility of a commercial gasoline.

Finally, Fig. 4 illustrates the effect of a change in engine conditions on the effectiveness of lead tetraethyl on a given gasoline. The only change involved is that from 600 r.p.m. and 212° F. jacket temperature to 900 r.p.m. and 362° F. This test is, of course, a plain comparison of the leaded fuels with heptane-octane mixtures, and does not indicate whether the lead is losing effectiveness or whether the heptane-octane blends are improving. At any rate, in relation to heptane-octane, lead tetraethyl is more effective at 900 r.p.m. and 362° than at 600 r.p.m. and 212°, and the curve is fairly typical of commercial gasolines.

The illustrations given above cover the best-known cases where relative anti-knock values are affected by the fuel or by the engine conditions, and give a fair idea of the magnitude of the effects involved. As mentioned before, these effects emphasize the necessity of keeping in mind that accurate figures of relative anti-knock values are significant only under a given set of conditions. However, with the exception perhaps of the very large effect of changes in air-fuel ratio on the anti-knock value of metal carbonyls, the figures given in Table I may be taken as reasonably correct.

Commercial Anti-knock Compounds

The commercial value of anti-knock agents is a complex function of their effectiveness, their cost, and some of their other properties, such as stability, freedom from harmful effects on human beings or engines, &c. Accordingly, of all the compounds mentioned above, only the following have ever been seriously considered for commercial use: (*a*) aniline (and the other aromatic amines), (*b*) iron carbonyl, and (*c*) lead tetraethyl. These will be discussed separately.

(*a*) **Aniline and Aromatic Amines.** In concentrations ranging from 2 to 6% approximately these compounds have enough anti-knock effect to be of practical value. One of their drawbacks is their low solubility in some hydrocarbons, especially in the highly paraffinic types of straight-run gasolines, where on account of the low octane number the use of anti-knock compounds is of particular interest. No accurate figures can be given for the solubilities because they vary so greatly with the fuels. Aniline itself is one of the least soluble aromatic amines. At room temperature it will dissolve to the extent of about 2% in straight paraffinic fuels, and up to 5% or more in some naphthenic or olefinic (cracked) fuels. Toluidine, xylidine, &c., are more soluble, and some substituted aromatic amines are completely miscible with most gasolines. A further obstacle to the use of aromatic amines is their objectionable odour, which is very noticeable wherever spillage of the gasoline occurs, as well as in the exhaust of the engine.

Aniline is the cheapest anti-knock compound of the group, not only per unit weight, but also per unit of anti-knock effect. Its concentrated solutions are toxic, absorption taking place by breathing as well as by skin contact. Its widespread use in motor fuels would accordingly necessitate strict observance of adequate safety measures. Aniline could probably be used satisfactorily, but the cost would be considerably higher than that of lead tetraethyl.

(*b*) **Iron Carbonyl.** Several iron carbonyls are known. The one which is used as an anti-knock compound is the pentacarbonyl, $Fe(CO)_5$. It is prepared by interaction of CO and sponge iron around 200° C. under 100–200 atm. pressure [26, 1930]. It is a colourless liquid of d^{20} 1·45 and boiling at 104° C. Like aniline, it is toxic, and strict precautions must be observed in handling its concentrated preparations. Iron carbonyl was used commercially in Germany for several years. It was shipped as 'Motyl', which was a 50 : 50 mixture with kerosine. The treated gasoline contained 0·5% or less of $Fe(CO)_5$, and was sold under the name 'Motaline'.

While its cost was low, one of its drawbacks was that the carbonyl decomposed rapidly when the gasoline was exposed to light. Difficulties were also encountered due to the short circuiting of sparking-plugs, caused by the deposition of magnetic oxide, Fe_3O_4, on the porcelain insulator. Extensive engine tests in the U.S.A. showed that the precipitation of iron oxides, particularly in the crankcase oil, lead to excessive engine wear.

Lead Tetraethyl. Lead tetraethyl is the only anti-knock compound which is used extensively at present. It is manufactured by the process invented by Kraus and Callis [18, 1926], by interaction of a lead-sodium alloy with ethyl chloride. The alloy is prepared by melting lead and sodium together in the right proportions and casting. The alloy, which is very brittle, is crushed to pea size and treated in an autoclave with ethyl chloride. The lead tetraethyl is steam-distilled out of the reaction mass and is then ready for use without further treatment.

Lead tetraethyl is a colourless liquid $d = 1{\cdot}65$, boiling around 200° C. (with some decomposition) under 760 mm. pressure, and distilling undecomposed either with steam or under reduced pressure. For use as an anti-knock agent, it is mixed with a bromine compound, ethylene dibromide, sometimes with the addition of a chlorine compound, such as ethylene dichloride [22, 1926]. The purpose of this addition is to limit the formation of lead oxide, which tends to accumulate in the combustion chamber, and to cause the conversion of the lead into lead bromide and chloride, which are removed from the engine. Enough gasoline-soluble dye is added to the mixture to impart a marked colour to the gasoline to which it is added. This mixture is sold under the trade name 'Ethyl' by the Ethyl Gasoline Corporation, under licences of the General Motors Corporation, the owners of the patents covering the use of lead tetraethyl as an anti-knock agent. In former years monochloronaphthalene was added in small amounts to the ethyl fluid, in order to promote lubrication of exhaust valve stems [23, 1928], but more recent tests have shown this to be superfluous and the monochloronaphthalene is no longer used.

The concentration of lead tetraethyl in ethyl fluid varies when the composition of the fluid is changed. Since the anti-knock value is due to the lead tetraethyl only, the concentrations in the finished gasoline are always expressed in terms of lead tetraethyl and not of fluid. This is expressed as c.c. $PbEt_4$/U.S. gal., c.c. $PbEt_4$/Imp. gal., or as c.c. $PbEt_4$/litre.

Ethyl fluid is shipped in tank cars or in 55-gal. steel drums, and also, in special cases, in 1-litre cans. It is mixed with gasoline at the refineries or bulk storage-points by means of special pumping installations embodying all the necessary safety appliances to preclude exposure of the workmen to the concentrated fluid. The concentration of lead tetraethyl in the finished gasoline is varied to suit the needs, but is not allowed in commercial gasolines to exceed 3·0 c.c./U.S. gal. (3·6 c.c./Imp. gal. or 0·80 c.c./litre). Extensive tests and field surveys covering a period of years have shown conclusively that at this low concentration the presence of lead in the gasoline does not constitute a health hazard to either gasoline handlers or the general public [9, 1930; 15, 1934; 19, 1926].

Analytical Methods

The presence of anti-knock compounds in a fuel cannot be detected by engine rating unless the octane number of the fuel itself is known. In the case of metallic compounds inspection of the engine after operation will usually disclose the presence of deposits in which the particular metal used can readily be identified. The usual anti-knock compounds differ widely chemically from most fuels, and can, therefore, be detected or determined quantitatively quite readily by chemical means.

Aniline and Aromatic Amines. The fuel is shaken with dilute hydrochloric acid, and the acid layer is separated and made alkaline. The amine separates out, and can be isolated by ordinary laboratory methods, identified and determined quantitatively. When aniline itself is suspected or known to be present it can be determined quantitatively, after extraction from the gasoline, by titration with bromine (preferably in the form of bromide-bromate solution) [10, 1926] according to the equation

$$C_6H_5NH_2+6Br = C_6H_2Br_3NH_2+3HBr,$$

and it can be further identified by the analysis and melting-point (119° C.) of the insoluble 2, 4, 6-tribromoaniline.

Metal Compounds. When exposed to strong light, gasolines containing metal carbonyls or organo-metallic compounds give a precipitate in which the metal can be identified by the classical methods [17, 1932]. The reaction is particularly rapid and sensitive in the case of carbonyls. These compounds can also be precipitated by treating the gasoline with chlorine, bromine, acid chlorides, &c.

Aborn and Brown [1, 1929] have shown that when lead is known to be the only heavy metal present in a sample of gasoline, it may be determined quantitatively by comparing the X-ray absorption of the gasoline with that of a known standard. This method has not yet been developed to the point where it can be used readily for routine analysis.

Volatile metal compounds can be differentiated from soluble but non-volatile compounds by distilling the gasoline (preferably under reduced pressure to minimize decomposition of the metal compound), and analysing for the metal in the distillate.

Specific methods for the quantitative determination of iron carbonyl and lead tetraethyl in gasoline are given below.

Determination of Iron Carbonyl in Gasoline. The method is based on the conversion of the carbonyl into ferric hydroxide by means of H_2O_2 and NH_3.

25 c.c. of the gasoline is pipetted into 200 c.c. of denatured alcohol contained in a 400-c.c. beaker. Concentrated aqueous ammonia and 3 c.c. of 30% hydrogen peroxide are added under constant stirring. The flocculent brown precipitate is allowed to settle and is filtered on paper moistened with alcohol. After washing with alcohol followed by hot water, the iron is determined quantitatively by any classical method.

Determination of Lead Tetraethyl in Gasoline [7, 1929]. The method is based on the conversion of the lead into lead bromide, and subsequent determination either gravimetrically as lead chromate, or volumetrically by titration with ammonium molybdate.

(*a*) **Gravimetric.** Measure with a pipette 100 c.c. of gasoline containing lead tetraethyl in a 400-c.c. beaker. Add slowly a solution of 30% bromine in carbon tetrachloride, until the permanent brown-red colour of bromine is obtained. Filter promptly through asbestos in a dry Gooch crucible (or through a fritted Jena glass filter crucible of no. 2 porosity) and wash with petroleum ether. Put the crucible back in the beaker where the precipitation was made and add about 3 c.c. of nitric acid (sp. gr. 1·40) in the crucible. Add a warm solution of 10% nitric acid in quantity just sufficient to cover the top of the crucible, bring to boiling, remove the crucible, and boil down to about 3 c.c. Dilute and filter the solution through soft filter-paper (if a Gooch crucible was used), rinsing the beaker and crucible with warm water. Just neutralize the filtrate with ammonium hydroxide and add 5 c.c. of 50% acetic acid. Now add slowly and with constant stirring 40 c.c. of a 5% solution of potassium dichromate. Stir for 5 minutes while the solution is boiling, then remove from the hot plate and keep in a warm place for 1 hour. Collect the precipitate on a weighed and ignited Gooch crucible and wash well with hot water. Dry in a crucible air-bath, or in an oven at 105° C., and weigh as lead chromate.

(*b*) **Volumetric.** Prepare the ammonium acetate solution as in method (*a*), boil down to 150 c.c., and titrate hot with a standard molybdate solution until a yellow coloration is obtained with tannic acid used as outside indicator. The molybdate solution is standardized against a known weight of lead or lead chloride. The indicator used is a 0·5% freshly prepared solution of tannic acid. Care must be taken always to use the same amount of indicator (2 drops) and solution (4 drops). A blank is run on the same amount of water and ammonium acetate, and the amount of molybdate solution used to give a distinct coloration (about 0·3 c.c.) is subtracted from the result of the titration.

Note 1. Gasolines containing a high percentage of unsaturated compounds absorb bromine vigorously with evolution of heat. In such cases it is highly advisable to dilute the sample with about 100 c.c. of a volatile petroleum fraction fairly free from unsaturated compounds, to add the bromine slowly, and to keep the beaker in ice. When this precaution is not taken, the results are apt to be low. Suitable diluents are, for instance, fighting-grade aviation gasoline, petroleum ether, and ligroin.

Note 2. The molybdate solution may be made to contain 2·380 g. of commercial C.P. salt per 1,000 c.c., in which case 1 c.c. of this solution used on an original 100 c.c. sample of gasoline corresponds to 0·1 c.c. of lead tetraethyl (sp. gr. 1·65) per U.S. gallon of gasoline.

Note 3. In some cases the lead nitrate which begins to precipitate when the solution is concentrated to 3 c.c. volume is contaminated by a small amount of organic matter. It is then advisable to evaporate to dryness and to treat with fuming nitric acid, repeating the operation until a clean white residue of lead nitrate is obtained.

REFERENCES

1. Aborn, R. H., and Brown, R. H. *Ind. Eng. Chem.*, Anal. Ed. **1**, 26 (1929).
2. Alden, R. C. *Nat. Petr. News*, **24**, no. 3, 33 (1932).
3. Beatty, H. A., and Edgar, G. *J.A.C.S.* **56**, 107 (1934).
4. Berl, E., and Winnacker, K. *Chal. and Ind.* **11**, 23 (1920).
5. Boyd, T. A. *Ind. Eng. Chem.* **16**, 894 (1924).
6. Charch, W. H., Mack, E., Jr., and Boord, C. E. *Ind. Eng. Chem.* **18**, 335 (1926).
7. Edgar, G., and Calingaert, G. *Ind. Eng. Chem.*, Anal. Ed. **1**, 221 (1929).
8. Egerton, A. C. B.P. 279,560 (29 July 1926); U.S.P. 1,771,169 (12 July 1930); *J.I.P.T.* **13**, 244 (1927).
9. *Final Report of the Departmental Committee on Ethyl Petrol* (Ministry of Health, London, 1930).
10. Francis, A. W. *Ind. Eng. Chem.* **18**, 821, 1095 (1926).
11. Gill, F. C., Mardles, E. W. J., and Tett, H. C. *Trans. Faraday Soc.* **24**, 574 (1928); Mardles, E. W. J., ibid. **27**, 681 (1931).
12. Gilman, H., and Balassa, L. *Iowa State Coll. Journ. Sci.* **3**, 105 (1929).
13. Hebl, L. E., Rendel, T. B., and Garton, F. L. *J.I.P.T.* **18**, 526 (1932); *Ind. Eng. Chem.* **25**, 187 (1933).
14. *Int. Crit. Tables, II*, 63; Campbell, J. M., Lovell, W. G., and Boyd, T. A., *J.S.A. Eng.* **26**, 163 T (1930).
15. Kehoe, R. A., Thamann, F., and Cholak, J. *J. Ind. Hygiene*, **16**, 100 (1934).
6. Kettering, C. F., and Midgley, T., Jr. U.S.P. 1,635,216 (12 July 1927).
17. Kiemstedt, H. *Erdöl und Teer*, **8**, 253 (1932).
18. Kraus, C. A., and Callis, C. C. Canadian P. 266,140 (23 Nov. 1926); U.S.P. 1,612,131 (28 Dec. 1926).
19. Leake, J. P., *et al.* *U.S. Pub. Health Bull.* no. 163 (1926).
20. Lovell, W. G., Campbell, J. M., Signaigo, F. K., and Boyd, T. A. *Ind. Eng. Chem.* **27**, 593 (1935).
21. Midgley, T., Jr. U.S.P. 1,573,846 (23 Feb. 1926).
22. —— U.S.P. 1,592,954 (20 July 1926).
23. —— U.S.P. 1,668,022 (1 May 1928).
24. Midgley, T., Jr., and Boyd, T. A. *J.S.A.E.* **15**, 659 (1920).
25. —— —— *Ind. Eng. Chem.* **14**, 589, 849, 894 (1922); **15**, 421 (1923).
26. Müller-Cunradi, M. U.S.P. 1,828,376 (20 Oct. 1930). See also Frydländer, J. H. *Rec. Trav. Chim.* **29**, 1 (1926).
27. Thole, F. B., and Stansfield, R. *J.I.P.T.* **18**, 526 (1932).

12. LEAD SUSCEPTIBILITY OF GASOLINE

By F. H. GARNER, Ph.D., F.I.C., M.I.A.E., M.Inst.P.T.
Anglo-American Oil Company Ltd.

THE rise in octane number of gasolines produced by the addition of a fixed proportion of lead in the form of tetraethyl lead varies with the type of gasoline, and the term 'lead susceptibility' has been proposed to describe this property. In a paper published in [10] 1929 it was shown that the effect of lead on gasolines varies with spirits from different sources: the addition of 1 c.c. of lead per gallon raised the compression ratio of one gasoline by 1·04, whereas with another gasoline of the same H.U.C.R. (a benzole blend), the addition of 1 c.c. of lead raised the compression ratio by only 0·7.

Hebl and Rendel [7, 1932] determined the lead susceptibility of a wide range of gasolines using the Ricardo E. 35 engine and recording the results in H.U.C.R. These authors suggested the relationship $I = SNK$ to express the improvement in H.U.C.R. as an exponential function of the concentration of lead tetraethyl, where

I is the increase in H.U.C.R.,
S is a measure of the steepness of the curve, i.e. lead susceptibility,
N is the number of millilitres of lead tetraethyl added to 1 gallon (U.S.) of gasoline,
K is a constant which represents the curvature of the line.

K for a series of some 60–70 gasolines did not vary appreciably from the figure of 0·75. They proposed the relationship

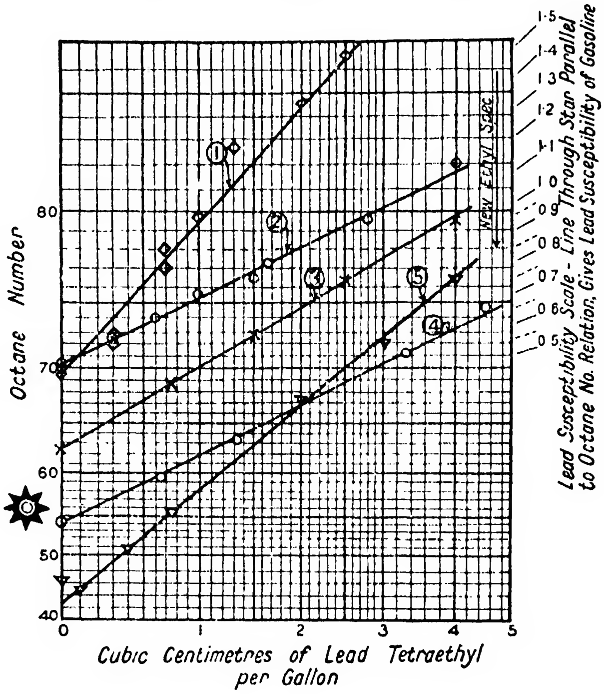
$$S = \frac{1}{0{\cdot}75\,N}$$

as a measure of the lead susceptibility of the gasolines, and thus from the H.U.C.R. of the gasoline and a mixture of the gasoline with one concentration of lead tetraethyl the lead susceptibility (S) of the gasoline is known. For different gasolines S ranged from 0·22 for Roumanian gasoline to 0·54 for Californian gasoline. They found that the lighter gasolines were exceptional in that they had a high H.U.C.R. and also a high lead susceptibility. Cracked gasolines in general had a low lead susceptibility.

In a further paper by Hebl, Rendel, and Garton the effect of lead tetraethyl on octane number (C.F.R. Research Method) was investigated [8, 1933]. The following five factors are stated to determine the octane number of any ethylized gasoline:

(1) The effectiveness of iso-octane in different concentrations in raising the anti-knock value of iso-octane/heptane mixtures;
(2) The effectiveness of lead tetraethyl on the gasoline in different concentrations;
(3) The octane number of the base gasoline;
(4) The lead susceptibility of the gasoline;
(5) The number of cubic centimetres of lead tetraethyl added per gallon of gasoline.

In this work they found certain gasolines (West Texas straight-run) which, when heavily treated with acid, showed no lead susceptibility for the first few cubic centimetres of lead tetraethyl added. In one case the addition of 4½ c.c. of lead tetraethyl produced no rise in octane number, but after this point further additions of lead produced a normal rise in octane number. In the following chart, taken from their paper, is plotted the octane number against lead additions (per U.S. gallon); the scales are chosen so that straight lines are obtained. Natural gasoline (No. 1) shows a much more marked lead susceptibility than cracked gasoline (No. 2). It will be noted that in nearly all cases the experimental data can be represented by a straight line. These authors point out that the lead susceptibility of a gasoline is determined not only by the hydrocarbons present, but may be markedly affected by small amounts of impurities either found in the gasoline or formed during treatment.



Ethyl blending chart. (Data obtained on several gasolines using C.F.R. engine at 212° F. (100° C.) jacket temperature and 600 r.p.m.) 1. Stabilized natural gasoline. 2. Cracked gasoline. 3. 50% cracked+50% West Texas straight-run gasoline. 4. West Texas straight-run gasoline. 5. Mid-Continent straight-run gasoline.

R. C. Alden [1, 1932] gave figures for octane number of gasolines with no lead content and also after the addition of 2 c.c. of lead tetraethyl. These confirm the high lead susceptibility of natural gasolines.

E. Endo [4, 1934] determined the lead susceptibility of 12 gasolines, using the Armstrong engine. It was found that the addition of methyl mercaptan had no effect on the lead susceptibility although other sulphur compounds diminished anti-knock value. Cracked gasolines gave an improved lead susceptibility. The presence of organic sulphur compounds has a marked effect in lowering the lead susceptibility of gasolines [9, 1935]. Organic disulphides, with the exception of carbon disulphide, were found to produce the greatest reduction in lead susceptibility, sulphides less, and cyclics the least effect on lead response. In general, reduction of sulphur content of gasolines effected substantial improvement in lead response, and an instance is quoted of a cracked gasoline in which the reduction of sulphur from 0·086% to 0·072% resulted in a saving at 70 octane number of 0·65 c.c. of lead per gallon.

Lead Susceptibility of Hydrocarbons

The effect of lead tetraethyl in a concentration of 1 c.c. per imperial gallon is recorded by Garner, Wilkinson, and Nash [6, 1932] in increasing the octane number of 20% solutions of five olefines, ranging from pentene to nonene in a base fuel. Similar data were recorded by Garner and Evans [5, 1932] on 21 hydrocarbons, including aromatics, cyclohexane, and cyclopentane in 20% solution. A few results reported at higher jacket temperature, namely, 300° F., as against 212° F., showed that lead was more effective at the higher temperature.

More recently, Boyd and co-workers [3, 1935] have made quantitative measurements of the specific anti-knock effect of lead tetraethyl on 62 individual hydrocarbons as measured by the addition of lead tetraethyl in a concentration of 1 c.c. per U.S. gallon. The table below summarizes their work:

Compound	*Critical compression ratio*	*Increase in critical compression ratio for addition of 1 c.c. of lead tetraethyl per gallon*
Paraffin Hydrocarbons		
n-Pentane	3·8	0·50
2-Methylbutane	5·7	0·95
n-Hexane	3·3	0·20
n-Heptane	2·8	0·20
3-Ethylpentane	3·9	0·20
2,4-Dimethylpentane	5·0	0·80
2,2,4-Trimethylpentane	7·7	2·10
2,7-Dimethyloctane	3·3	0·20
3,4-Diethylhexane	3·9	0·30
Olefine Hydrocarbons		
1-Pentene	5·8	0·30
2-Pentene	7·0	0·50
2-Methyl-2-butene	7·0	0·70
Dimethylbutadiene	8·6	0·10
2,4-Hexadiene	6·6	0·10
1,5-Hexadiene	4·8	0·25
1-Heptyne	4·9	0·33
3-Heptyne	3·4	0·10
1-Heptene	3·7	0·25
3-Heptene	4·9	0·80
3-Ethyl-2-pentene	6·6	0·50
2,4-Dimethyl-2-pentene	8·8	0·70
2-Methyl-5-hexene	4·7	0·25
3-Methyl-5-hexene	5·0	0·20
2-Octyne	4·0	0·10
1-Octene	3·4	0·15
2,2,4-Trimethyl-3-pentene	10·0	0·35
2,2,4-Trimethyl-4-pentene	11·3	0·25
Naphthene Hydrocarbons		
Cyclopentane	10·8	2·70
Cyclohexane	4·5	0·65
Methylcyclohexane	4·6	0·30
Cyclohexylacetylene	4·6	0·21
1,2-Dimethylcyclohexane	5·1	0·35
1,3-Dimethylcyclohexane	4·4	0·21
1,2-Methylethylcyclohexane	4·3	0·16
1,3-Methylethylcyclohexane	3·8	0·12
1,4-Methylethylcyclohexane	3·7	0·13
1,2-Methyl-*n*-propylcyclohexane	3·6	0·13
1,3-Methyl-*n*-propylcyclohexane	3.4	0·12
1,4-Methyl-*n*-propylcyclohexane	3·3	0·12
1,4-Methylisopropylcyclohexane	4·0	0·26
Naphthene Hydrocarbons (cont.)		
1,2-Methyl-*n*-butylcyclohexane	3·4	0·10
1,3-Methyl-*n*-butylcyclohexane	3·3	0·10
1,4-Methyl-*n*-butylcyclohexane	3·2	0·10
1,2-Methyl-*n*-amylcyclohexane	3·2	0·10
Decahydronaphthalene	3·6	0·13
Aromatic Hydrocarbons		
Phenylacetylene	12·4	−0·80
Ethylbenzene	10·5	2·00
Benzylacetylene	7·4	0·12
Methylphenylacetylene	11·8	−0·30
1,4-Methylisopropylbenzene	11·1	1·00
1-Phenylbutadiene	9·5	0·00
tert-Amylbenzene	12·1	2·00
Trimethylphenylallene	8·3	−0·20
Unsaturated Cyclic Hydrocarbons		
Cyclopentadiene	10·9	−0·90
Dimethylfulvene	9·2	−0·13
Indene	11·2	−0·10
Dicyclopentadiene	11·0	−0·30
Cyclopentene	7·9	0·20
1,3-Cyclohexadiene	5·9	−0·02
Cyclohexene	4·8	0·20
Dipentene	5·9	0·25

It was shown that lead tetraethyl exhibited a very wide range of effectiveness depending on the structure and properties of the hydrocarbon. Whereas gasolines show a range on this scale of from 0·1 to 0·3, the hydrocarbons investigated range from −0·8 to 0·9 for cyclopentadiene to +2·7 for cyclopentane. It will be noted that certain of the unsaturated cyclic and aromatic hydrocarbons have negative lead susceptibilities, that is, the addition of lead caused a decrease in the compression ratio for incipient knock. The relationship between critical compression ratio and lead susceptibility is of special interest; (*a*) for paraffins and naphthenes, the higher the critical compression ratio the greater the lead susceptibility; (*b*) for olefines and acetylenes, increase in compression ratio produces no marked change in lead susceptibility; and (*c*) for unsaturated cyclics, increase in compression ratio produces a decline in lead susceptibility. A few aromatic hydrocarbons which were investigated were found to show relatively high lead susceptibilities.

The Effect of Sulphur Content on Lead Response

Birch and Stansfield [2, 1936] have investigated the effect of sulphur compounds on lead susceptibility in a series of blends containing 0·1% sulphur, and they found that the effect on lead susceptibility increased as follows: carbon bisulphide, thiophen, sulphides, mercaptans, disulphides, and trisulphides. Certain sulphur compounds are themselves definitely pro-knock, particularly ethyl trisulphide and the mercaptans, whilst others, as, for example, the sulphides, have no measurable effect. Blends of heptane with olefines and diolefines showed a poor lead susceptibility when 0·1% of sulphur and ethylene disulphide were added. It is considered that these results throw some light on the poor lead susceptibility shown by certain gasolines containing cracked distillates. Experiments on straight-run Iranian and Venezuelan gasoline indicate that a considerable saving in lead tetraethyl might be effected by thorough desulphurization.

REFERENCES

1. ALDEN, R. C. *Nat. Petr. News*, 20 Jan. 1932, p. 36.
2. BIRCH, S. F., and STANSFIELD, R. *Ind. Eng. Chem.* **28**, 668 (1936).
3. CAMPBELL, J. M., SIGNAIGO, F. K., LOVELL, W. G., and BOYD, T. A. *Ind. Eng. Chem.* **27**, 593 (1935).
4. ENDO, E. *J. Fuel Soc. Japan*, **13**, 22 (1934) (*J.I.P.T.* **20**, 430 A (1934)).
5. GARNER, F. H., and EVANS, E. B.. *J.I.P.T.* **18**, 751 (1932).
6. GARNER, F. H., WILKINSON, R., and NASH, A. W. *J.S.C.I.* **51**, 265 T (1932).
7. HEBL, L. E., and RENDEL, T. B. *J.I.P.T.* **18**, 187 (1932).
8. HEBL, L. E., RENDEL, T. B., and GARTON, F. L. *Ind. Eng. Chem.* **25**, 190 (1933).
9. SCHULZE, W. A., and BUELL, A. E. *Nat. Petr. News*, **27**, no. 41, 25 (1935).
10. STANSFIELD, R., and THOLE, F. B. *Ind. Eng. Chem.*, Anal. Ed. **1**, 102 (1929).

13. OXIDANTS AND ANTI-OXIDANTS IN THE PETROLEUM INDUSTRY

By E. W. J. MARDLES, D.Sc., F.I.C.
Air Ministry Laboratory (Royal Aircraft Establishment)

OXIDANTS and anti-oxidants within the past few years have reached a position of considerable importance in the petroleum industry because it has been found possible by their powerful help, not only to produce better engine fuels and to stabilize lubricating oils, transformer oils, cracked spirits, &c., against deterioration by oxidation, but also to obtain valuable chemical products from petroleum as a raw material.

The economies effected by the use of anti-oxidants in gasoline in the United States already total at least five million dollars a year and they will be still greater when the advantages of this method of finishing gasoline are fully realized [58, 1934]; Hoffert and Claxton [79, 1934] in summarizing the advantages of using anti-oxidants in motor fuels, state that an increased yield of refined spirit varying from 3% to 30% is obtainable, there being also a considerable reduction in refining costs. An interesting example of the value of an anti-oxidant is mentioned by Ward, Jordan, and Fulweiler [145, 1933], who state that 150,000 gas stoppages were reported in one city alone in a single year due to the deposition of gum in the gas-meters; the trouble, which was found to be due to oxidation and polymerization of some of the constituent hydrocarbons of the gas, was minimized by the removal of sulphur compounds which acted as oxidants and by the use of an anti-oxidant, namely, a cresol solution of hydroquinone. Another well-known instance of the value of an anti-oxidant is the use of about 3 c.c. of lead tetraethyl per gallon of gasoline to raise the knock-rating; these 'leaded' fuels are of especial use for aeronautical high-compression boosted engines, which are liable to damage and failure if the ordinary petrols are employed.

As the names imply, oxidants are substances which promote oxidation and combustion, whilst, on the other hand, anti-oxidants inhibit or retard oxidation changes. With their use it has been found possible to control the oxidation and combustion of petroleum hydrocarbons, both by altering the rate of reaction and by lowering or raising the temperature of self-ignition and of incipient oxidation; thus, although methane is exceptionally resistant to oxidation by atmospheric oxygen at normal pressure, temperatures ranging from 700° to 1,000° C. being given in the literature as necessary for the reaction to occur when there is little opportunity for surface reaction to come into play, yet when a little ozone is added to the air or a catalytic surface introduced into the reaction chamber, the oxidation of methane into formaldehyde, methyl alcohol, &c., can proceed at as low a temperature as 250° C.

Positive and Negative Effects. Ozone is a well-known oxidant; it promotes violent knocking in the petrol engine to a like extent that lead tetraethyl, the familiar fuel anti-knock, known to be a powerful anti-oxidant in petrol vapour-air mixtures, delays it [25, 1933]. Usually, oxidants and anti-oxidants have decidedly opposite effects on the behaviour of a particular system; thus, for example, very small amounts of iron carbonyl, selenium diethyl, lead tetraethyl, and other anti-knock substances most often raise the self-ignition temperature of an explosive mixture, whilst iso amyl nitrite, nitrogen peroxide, &c., which promote knocking, can, when present in small amounts, lower the self-ignition temperature. In Table I are given a selection of data illustrating this behaviour.

Table I

(a) *Effect of organo-metallic compounds, &c. (0·1% wt.) on the self-ignition temperature of gasoline* [53]

Selenium diethyl	140° C. rise
Iron carbonyl	130° C. ,,
Lead tetraethyl	90° C. ,,
Nickel carbonyl	40° C. ,,
Bismuth triphenyl	42° C. ,,

(b) *Effect of iron carbonyl on self-ignition of gasoline* [10]

0·2%	31° C. rise
0·5%	57° C. ,,
0·7%	63° C. ,,
10·0%	59° C. ,,

(c) *Effect of anti-knock substances on the self-ignition temperature of gasoline* [146]

Substance	*Amount (g. per litre)*	*Effect*
Lead tetraethyl .	0·5	105° C. rise
,, ,,	1·0	130° C. ,,
Iron carbonyl . .	2·9	170° C. ,,
Aniline . . .	5·0	65° C. ,,
,, . . .	10·0	80° C. ,,
Tin tetraethyl . .	2·0	75° C. ,,
,, ,, . .	4·0	110° C. ,,

(d) *Effect of pro-knock substances on self-ignition of gasoline, &c.*

Substance	*Amount*	*Effect*
Silicon tetraethyl .	4 g. per litre	10° C. fall (Weerman) [146]
Nitrogen peroxide .	2·5% vol. in m. xylene	205° C. fall
,, ,,	2·5% vol. in n. butyl alcohol	235° C. ,,
,, ,,	5% vol. in n. butyl alcohol	355° C. ,,
Benzoyl peroxide .	2% in m. xylene	13° C. ,,
Iso amyl nitrite .	2% in m. xylene	68° C. ,,
,, ,, .	5% in m. xylene	100° C. ,,
,, ,, .	10% in m. xylene	128° C. (Mardles) [93]
Acetylene tetrabromide	10%	140° C. fall (Egerton and Gates) [53]

This positive and negative effect is again seen in experiments on flame speed; Nagai [108, 1930], found during an investigation on the effect of anti-knock materials on the speed of flame in a closed tube that 0·1% of tin tetramethyl, selenium diethyl, and other organic metallic compounds, markedly decreased the mean flame speeds; a similar behaviour with lead tetraethyl was observed by Souders and Brown [129, 1929], whilst, on the other hand, Prettre, Dumanois, and Laffitte [117, 1930] found that the pro-knock substance amyl nitrite accelerated the flame speed. Yoshikawa [152, 1931], who studied the homogenous oxidation of methane under high pressure, states that nitrogen peroxide (oxidant) greatly promoted the oxidation rate whilst lead tetraethyl (anti-oxidant) retarded it, there being little change in the composition of the condensed products. Schaad and Boord [123, 1929] found that lead tetramethyl, selenium diethyl, and other anti-knocks suppressed the slow combustion of toluene and kerosine, whilst propyl nitrite and other pro-knocks accelerated it; Layng and Youker [86, 1928] found a similar behaviour with lead tetraethyl and butyl nitrite on the slow combustion of heptane (cf. Article 1).

Sensitivity to Change of Conditions. It is necessary to point out in this connexion that the precise measurement of the effectiveness of anti-knocks can only be determined by engine experiments and not by any measurement of the change in self-ignition temperature or flame speed produced by an added substance; that is to say, any anti-oxidant must be tried out under the same or similar conditions in which it is to be employed. It is interesting to note that some investigators [100, 1929; 111, 1924; 69, 1929] report that lead tetraethyl can lower self-ignition temperatures and amyl nitrite raise them; whilst Egerton [50, 1928] and others found sometimes no change in flame speed (cf. Article 1). Townend and Mandlekar [141, 1933] report that the influence of lead tetraethyl on the self-ignition temperature of a 5% butane-air mixture is remarkably affected by pressure; thus, the increase caused by 0·05% lead tetraethyl was 49° at 1½ atmospheres, 160° at 1¾ atmospheres, and 47° at 2 atmospheres. These results illustrate the extreme sensitivity of oxidants and anti-oxidants to change of condition. It is possible that their principal effect is masked by a secondary or subsidiary effect; this will be discussed later.

Oxidants and Anti-oxidants compared with Catalysts.

Moureu and colleagues [106, 1928], from their extensive researches on oxidants and anti-oxidants, formed the opinion that one substance cannot be spoken of as an anti-oxidant and another as an oxidant, since whether they are positive or negative is dependent on the conditions of the experiment and not on the nature of the substance. They consider that the phenomenon of anti-oxidant activity is very general in character and contrary to the conclusion that might be drawn from a small number of isolated and apparently unconnected examples, anti-oxidant activity is widely distributed. In actual practice, it is exceptional to find an oxidizable system free from anti-oxidant impurities.

Anti-oxidants do not inhibit oxidation changes completely or delay self-ignition indefinitely; they can reduce the rate of reaction temporarily to an enormous extent, but when once they become used up, the reaction proceeds on its normal course. Similarly oxidants exert a definite increase in the rate of reaction dependent upon their concentration, but the effect ceases on their exhaustion. In this respect, they differ from the usual catalysts which remain unchanged after the reaction is completed. Oxidants and anti-oxidants are usually used up either by chemical reaction or combination during the time they function; thus, nitrogen peroxide or ozone used for stimulating the oxidation of petroleum hydrocarbons by atmospheric oxygen, in the effort to obtain useful oxidation products, lose oxygen and are reduced. Similarly organic peroxides, which are strong oxidants, become reduced to a lower oxide. Benzene vapour, which inhibits the vapour-phase oxidation of hexane, becomes autoxidized to phenol; ortho- and para-cresols used for inhibiting the gumming of coal carbonization spirits appear to form quinones. The organo-metallic compounds which act as anti-knocks decompose thermally before they function, the decomposition products being the actual anti-oxidants.

Mutual destruction of Oxidants and Anti-oxidants.

Oxidants and anti-oxidants offset their respective effects by reacting with each other; Egerton and Ubbelohde [55, 1934] have shown this to be the case with diethyl peroxide and lead tetraethyl in engine fuel, also Yamada [150, 1933] and Haslam and Frolich [73, 1927] have found a similar behaviour with anti-oxidants added to mineral oils containing organic peroxides. They also found that the anti-oxidants in oil were poisoned by copper. Anti-oxidants in cracked spirits are destroyed by organic peroxides [103, 1934]. The effectiveness of an anti-oxidant can also be reduced by the presence of relatively small quantities of impurities such as sulphur, chlorine, mineral acids, &c.; some fuels after acid wash appear to be poor in response to lead tetraethyl [76, 1933].

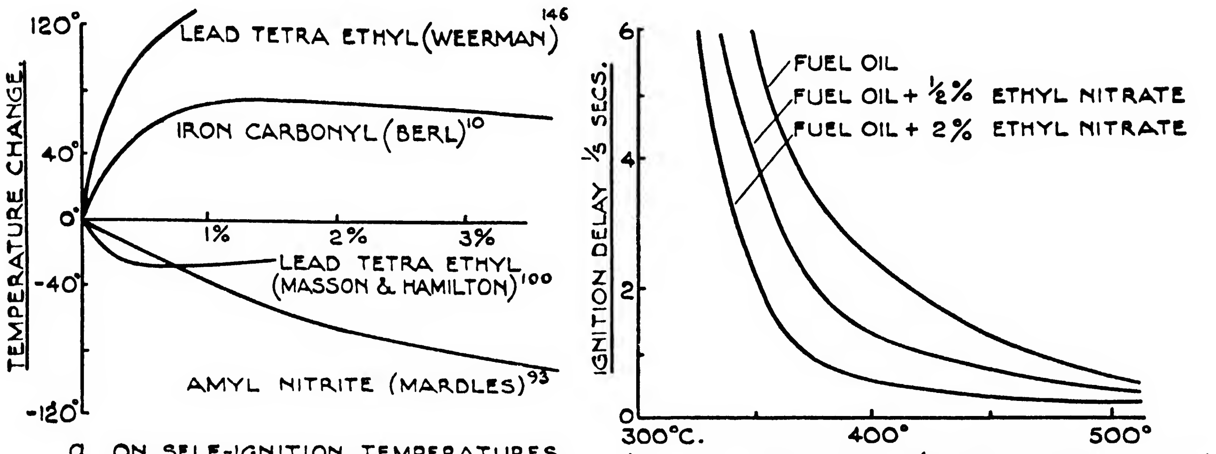
Concentration and Effect. From the effect of substances in increasing amounts on the self-ignition temperature given in Table I, and from Fig. 1, showing the influence of concentration on activity, it will be seen that with increasing concentration the effect of oxidants and anti-oxidants falls away, slowly at first and then rapidly, whilst in extreme cases the anti-oxidant becomes an oxidant. This phenomenon is especially found with lead tetraethyl in fuels; F. R. Banks states [7, 1934], for instance, that the first c.c. of lead tetraethyl added to a gallon of a particular gasoline may raise the anti-knock value of the gasoline by 10 octane numbers, the second c.c. may only give a further increase of 5 numbers, and the third an increase of 2 or 3, and so on, until no further increase is shown by additional amounts.

A similar behaviour of anti-oxidants has been observed with their use in cracked spirits, there often being an optimum amount for the anti-oxidant.

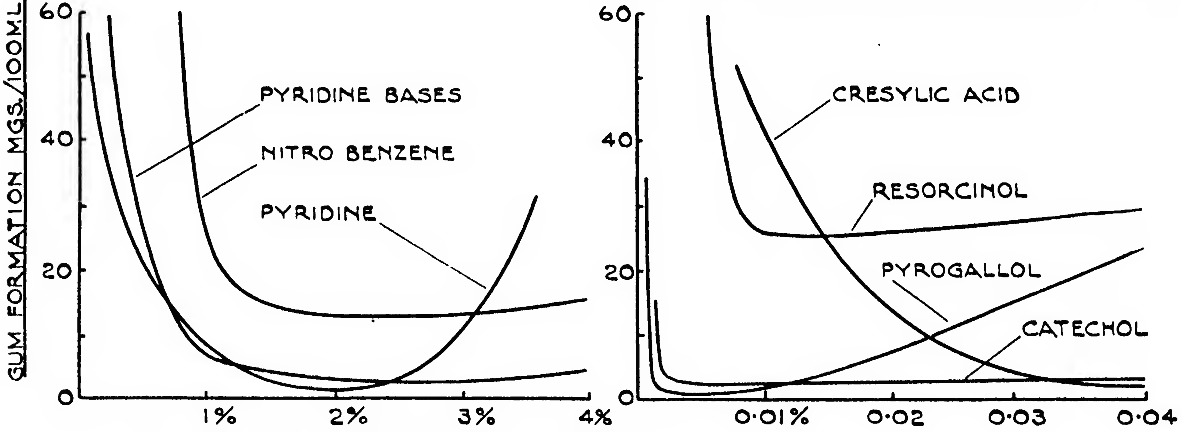
One of the recent problems arising from the modern use of cracked gasoline, coal carbonization spirit, shale spirit, and other fuel spirits which contain hydrocarbons of the olefinic or unsaturated classes, is the prevention of their deterioration by oxidation during storage, there being a fall in knock rating and an accumulation of gum in the fuel with time. Adventitious impurities in the fuel, such as iron rust or traces of mineral acids, promote oxidation, but, on the other hand, if one part in a hundred thousand of para-amino-phenol or hydroquinone be added, the normal storage life is often prolonged several fold.

Inversion of Anti-oxidants. The complexity of the problem can be judged from the fact that often an anti-oxidant becomes an oxidant and vice versa with change of circumstance. Mardles [94, 1931] has shown that iron carbonyl and lead tetraethyl, which are anti-oxidants in the case of petrol-air mixtures, can act as oxidants with methane, ethane, ethylene, and hydrogen in air (see Fig. 2). Naylor and Wheeler [109, 1933] found that the reactions occurring below the ignition temperature in mixtures of methane and air were retarded by traces of iodine, ethyl iodide, or ethyl bromide, whereas with ethane the corresponding reactions are accelerated by these substances. Similarly, nitrogen peroxide and iron carbonyl can inhibit the oxidation of amylene, pentane, or octane in the vapour phase. Mardles [94, 1931] and Lewis [90, 1930] found that 0·1% nitrogen peroxide increased the time lag preceding self-ignition from 3·6 to 16 sec., but that nitrogen peroxide promoted the oxidation of methane, paraffin wax, and other petroleum products and can act as a pro-knock in engine fuels; in liquid-phase oxidations iron carbonyl can often accelerate [96, 1929; 57, 1932]. Frequently there is an interchange of roles when the temperature is raised or when a certain stage has been reached during the course of a reaction.

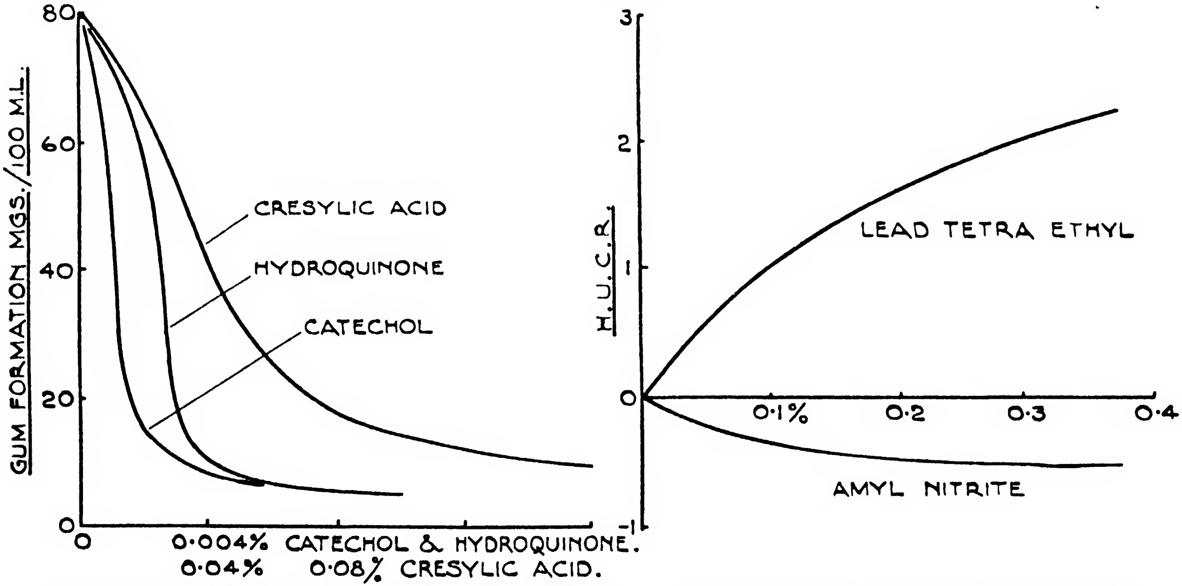
FIG. I RELATIONSHIP BETWEEN CONCENTRATION AND EFFECT.



a ON SELF-IGNITION TEMPERATURES   b. ON IGNITION DELAY (F. FOORD J.I.P.T. 18, 533. 1932)



C. & D. ON GUM FORMATION IN BENZOLE.



e. ON GUM FORMATION IN CRACKED SPIRIT. (THOMAS)138   f. ON KNOCK RATING OF PETROL. (CALLENDAR)32

FIG. 1.

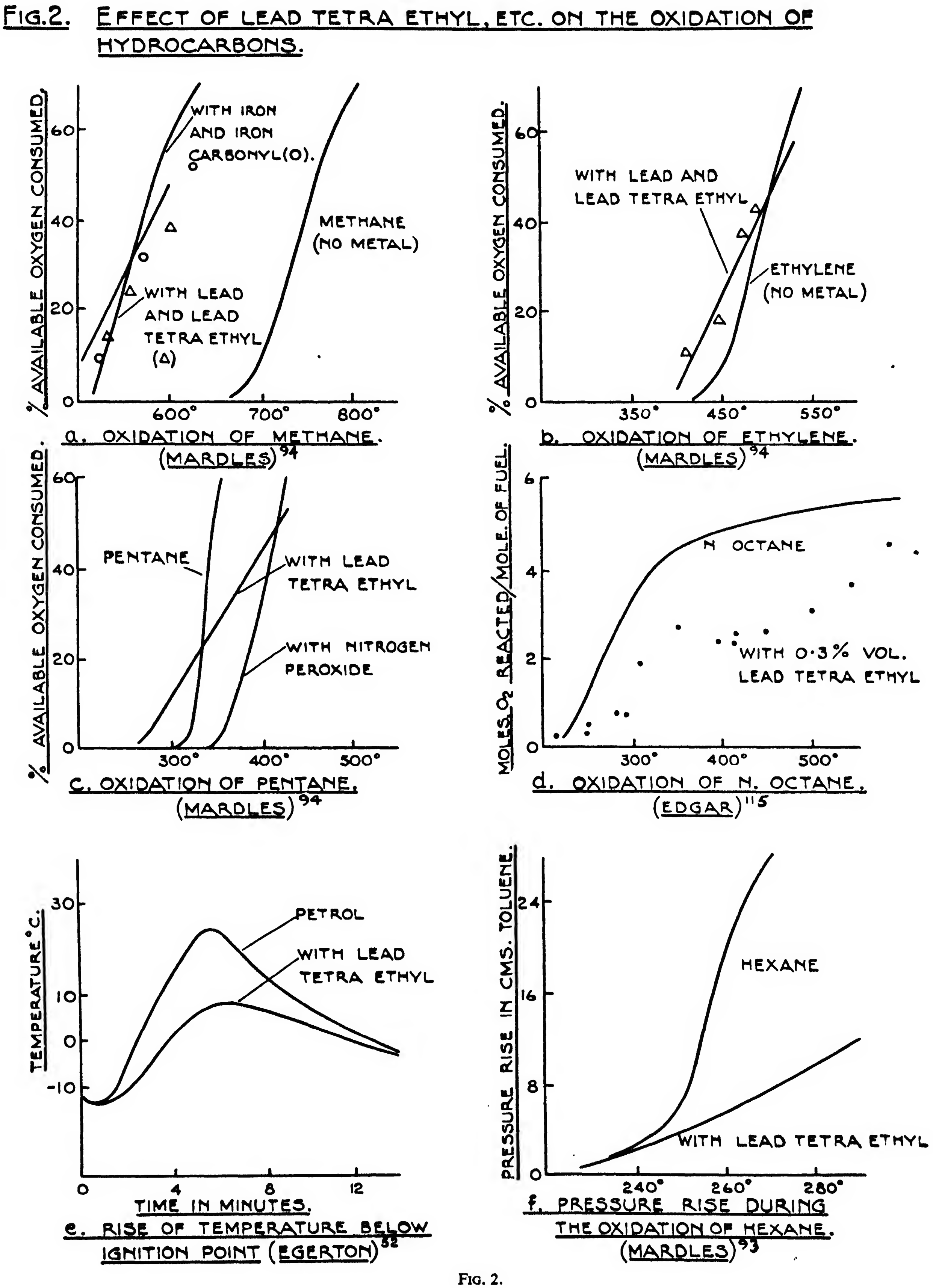


FIG. 2. EFFECT OF LEAD TETRA ETHYL, ETC. ON THE OXIDATION OF HYDROCARBONS.

a. OXIDATION OF METHANE. (MARDLES)[94]

b. OXIDATION OF ETHYLENE. (MARDLES)[94]

c. OXIDATION OF PENTANE. (MARDLES)[94]

d. OXIDATION OF N. OCTANE. (EDGAR)[115]

e. RISE OF TEMPERATURE BELOW IGNITION POINT (EGERTON)[52]

f. PRESSURE RISE DURING THE OXIDATION OF HEXANE. (MARDLES)[93]

FIG. 2.

In spite of the complexity and the apparent anomalies, definite conclusions have been reached with regard to the general mechanism of action of oxidants and anti-oxidants, more especially from the standpoint of molecular kinetics and chemistry of autoxidation. There still remains much to be done in order to unravel the complex sequence of chemical changes and to reconcile the conclusions of various investigators in the field of the organic chemistry of the oxidation and combustion changes.

Induction period in Oxidation and Combustion.

Several characteristic features of oxidation and combustion are now being intensively studied, and one of these subjects which has attracted great attention and is of special significance regarding oxidants and anti-oxidants is the so-called induction period. During this period apparently little occurs, but nevertheless the changes which do occur are important, since without them the main reaction cannot proceed.

Tizard and Pye [140, 1922] have shown that after adiabatic compression of an explosive mixture there is a definite period of induction before self-ignition occurs.

Similarly, Bone, Fraser, and Witt [17, 1924] have demonstrated that with mixtures of methane and oxygen after an electric spark has passed, there is a definite lag before combustion occurs. In the Diesel engine the lag period is manifested on the indicator diagram by a delay angle [88, 1931]: this delay can be reduced by the addition of a small percentage of an oxidant such as ethyl nitrate, amyl nitrite, acetaldehyde, and other substances of low self-ignition temperature.

Francis [64, 1922] has reported induction periods up to one month in the liquid-phase oxidation of paraffin wax at 100° with oxygen, there being apparently no change as indicated by iodine value determinations; when oxidation began, it did so with simultaneous formation of water, carbon dioxide, formic acid, &c. He found that moisture or the addition of a little turpentine decreased the induction period considerably.

A technical use of the measurement of the induction time has been made by the fuel-refiner for the purpose of appraising cracked spirits from the standpoint of storage properties. A sample of the fuel is placed in a bomb and is submitted to the action of compressed oxygen at 100° C.; the absorption of oxygen apparently does not occur at once, but there is a period of many minutes, the so-called induction period, during which the pressure remains constant. The stage of rapid oxidation of the fuel is accompanied by a correspondingly rapid fall in pressure. This is seen in Fig. 6*a*. The length of the induction period has been regarded by the users of the method as being roughly proportional to the stability of the fuel against oxidation. The effect on storage properties of the addition of an anti-oxidant to the fuel is judged by the increase in the induction period; thus, for example, Egloff and colleagues [59, 1932] found that a small addition of thiodiphenylamine increased the induction period from 45 minutes to 1,440 minutes, indicating a possible increase in the storage life of thirty-fold. Rogers, Bussies, and Ward [119, 1933], who studied the anti-oxidant effect of phenylaminophenol and alpha-naphthol on the oxidizability of cracked spirit, state that the effect was to increase the induction period in proportion to the amount used.

Bone and Hill [18, 1930], studying the oxidation of ethane in oxygen at 316° in a closed silica bulb, found an induction period, in this case about 30 minutes, during which no perceptible oxidation occurred. They found that the induction period was shortened considerably by introducing into the gas mixture some foreign vapour such, for example, as moisture, iodine, nitrogen peroxide, ethyl alcohol, or formaldehyde.

Effect of Oxidants and Anti-oxidants on Induction Period. In general, oxidants decrease the induction period whilst anti-oxidants increase it, sometimes to a considerable extent; this is shown in Figs. 3 and 4. Chebotar [41, 1934], who studied the oxidizability of lubricating oils, &c., in oxygen under pressure at 150°, found that beta-naphthylamine prolonged the induction period with the oil Nujol by 15 times and decreased the amount of oxidation by 60 times. Haslam and Frolich [73, 1927] found with 0·05% diphenylamine in a mineral oil that the induction time was increased from 2 to 10 hours (Fig. 4).

Similarly, Egloff and colleagues report that with 0·00005 mole inhibitor in 100 g. gasoline, whereas the induction period for the plain fuel was 45 minutes, pyrogallol increased it to 1,440 minutes, para-aminophenol to 1,470 minutes, alpha-naphthol to 1,920 minutes; benzoyl peroxide decreased the time to 35 minutes. They also found that the organic peroxides (well-known oxidants) formed in a cracked spirit by aeration, caused a marked decrease in the induction time, but when these were removed by passing through fuller's earth, the deleterious effects were eliminated.

Formation of Oxidants during Hydrocarbon Oxidation, Autocatalysis. Brunner and Rideal [27, 1928; 26, 1930] have studied the induction period during the vapour-phase oxidation of normal hexane. They discovered that important oxidation changes were occurring in the gas mixture, although these were not recorded by any large pressure difference. From analyses made of the gas mixture during the induction period, it seemed probable that a number of chemical reactions involving the formation of compounds containing active oxygen, such as organic peroxides, were taking place. When aniline vapour (0·3%) was present, the induction period was doubled and there was no evidence of the presence of peroxides until the aniline had been exhausted, when the normal reaction continued (Figs. 3 and 5).

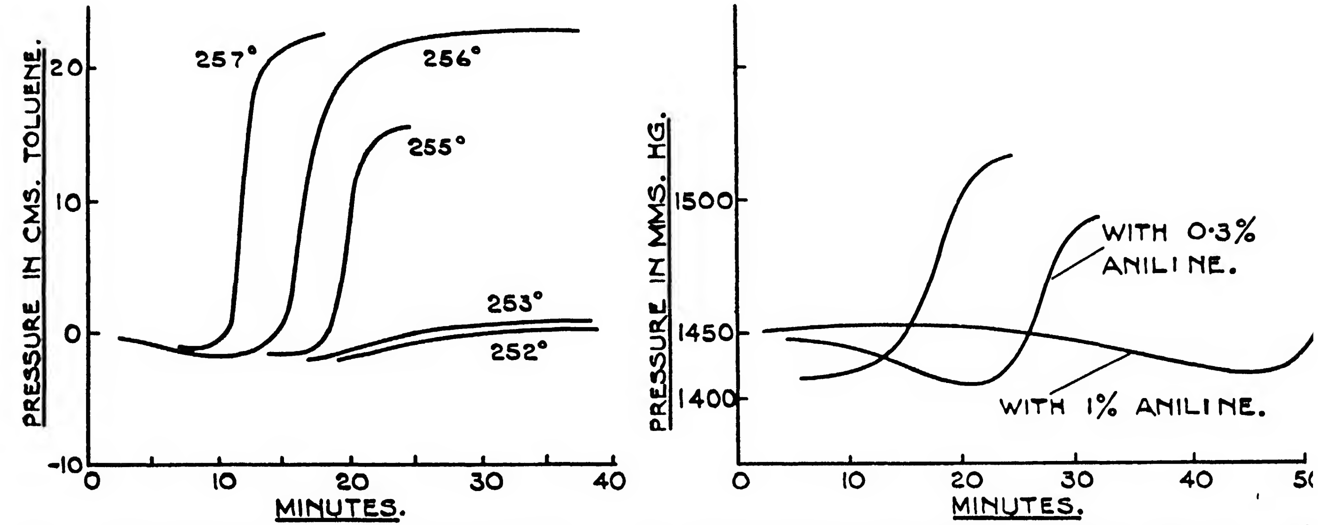
The significance of the appearance of peroxides in hydrocarbon oxidation and combustion has also been discussed by Callendar [32, 1927] and others with regard to engine knock, by Brooks [22, 1926] with regard to the oxidation of mineral oils, and by Moureu and colleagues with regard to anti-oxidant actions in general.

It would appear from this that the oxidation reactions in a hydrocarbon-oxygen system can occur with vigour only when certain reacting molecules are formed, that is to say, when the system produces its own oxidant or catalyst. Time is required for these oxidation products to accumulate and make their influence felt; if any addition is made to the system whereby the quantity of the oxidant is reduced or increased, there should be a corresponding reduction or increase, as the case may be, in the time of the induction period.

There are, however, known cases in combustion chemistry of the reverse to the above autocatalytic reactions, when the products of oxidation act as inhibitors; this is the case with carbon disulphide [45, 1925; 94, 1931], and hydrogen [116, 1933].

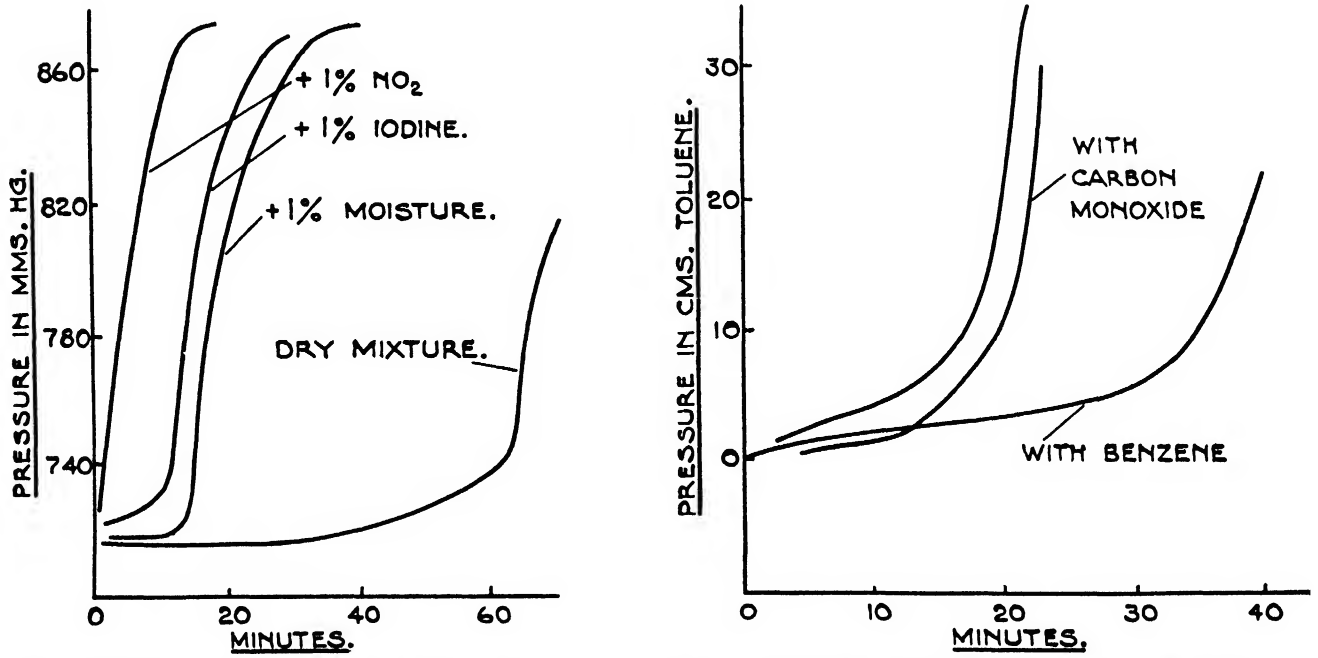
Confirmation of the hypothesis that the oxidation products of the hydrocarbons often act as their own oxidants

FIG. 3. INDUCTION PERIODS DURING VAPOUR PHASE OXIDATION AND THE EFFECT OF OXIDANTS AND ANTI-OXIDANTS.



a. HEXANE IN AIR. (MARDLES)[93]

b. HEXANE IN OXYGEN AT 210°C. (BRUNNER)[2]

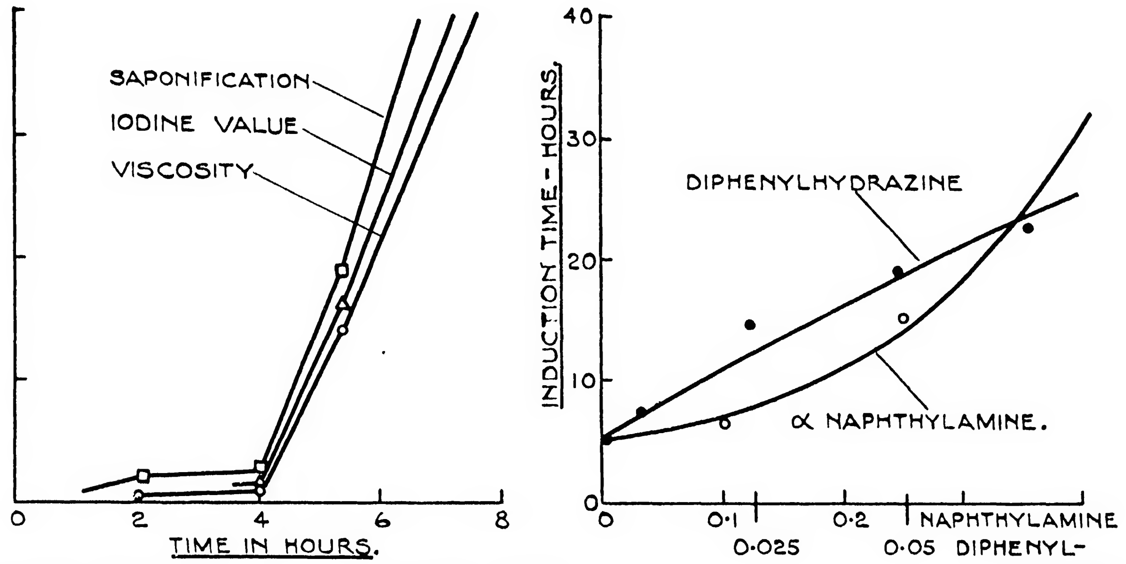


c. ETHANE IN OXYGEN AT 316° (BONE & HILL)[18]

d. CYCLOHEXANE IN AIR AT 295°C. (MARDLES)[93]

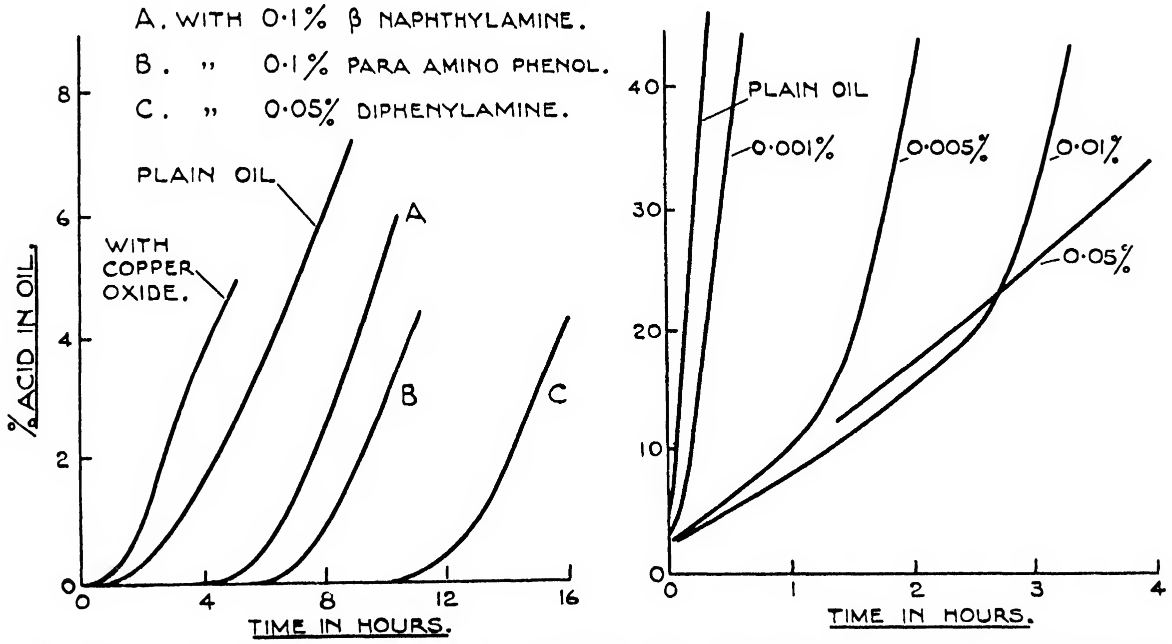
Fig. 3.

FIG. 4. INDUCTION PERIODS DURING LIQUID PHASE OXIDATION AND THE EFFECT OF OXIDANTS AND ANTI-OXIDANTS.



a. THE OXIDATION OF OLIVE OIL AT 100°C. (YAMAGUCHI)[151]

b. EFFECT OF ANTI-OXIDANTS ON INDUCTION TIME.



c. EFFECT OF SUBSTANCES ON DEVELOPMENT OF ACIDITY IN A MINERAL OIL AT 130°C. (HASLAM & FROLICH)[73]

d. CURVES SHEWING THE EFFECT OF INCREASING AMOUNTS OF RESORCINOL ON GUM FORMATION IN A BENZOL OXIDATION TEST AT 100°C. (HOFFERT & CLAXTON)[79]

FIG. 4.

is given by the results of the investigation now being carried out on the problem of stabilizing cracked spirits.

It is known that during storage or during the so-called induction period in the bomb method of appraising the stability of cracked spirits, peroxidation with formation of gum and development of acid is occurring [153, 1931; 103, 1934]. From Fig. 5, prepared from data obtained by Egloff and colleagues and by other investigators, it will be seen that peroxidation and deterioration of a cracked spirit are closely connected. Egloff considers that the peroxide number (gram-equivalents of active oxygen per 1,000 litres) is a convenient measure of the extent of gasoline deterioration and is significant, not alone because the formation of peroxides is important, but because the concentration of peroxides is an index to the entire complex series of reactions which go on when cracked gasoline is in contact with oxygen.

The effect of inhibitors (in this case, wood-tar distillate, catechol, &c.) was to postpone the organic peroxide formation, that is to say, the inhibitor was effective only in so far as it destroyed the oxidant by reacting or combining with it. When an inhibitor is present, peroxides form for a time at a very slow rate, but peroxide formation is not entirely eliminated. They build up at first at a fairly uniform rate, then at an increasing rate, probably as the inhibitor is becoming reduced in concentration, and finally with great rapidity. The rate of peroxide formation during the early part of the induction period and the inhibitor susceptibility appear closely related.

From experiments carried out by Dupont and Allard [49, 1930] with the use of hydroquinone as an anti-oxidant, they formed the opinion that the hydroquinone combined molecularly with the oxidant formed in the initial oxidation, so deactivating it, but not necessarily becoming oxidized.

Manning [92, 1934] found that 0·5% hydroquinone in coal spirit inhibited the formation of organic peroxides and the general deterioration by oxidation with formation of gum.

Confirmatory evidence on the significance of organic peroxides in the oxidation of petroleum products has been given by Wagner and Hyman [143, 1929] working on the lines of Brooks, and by Kogerman [84, 1927], Mardles and Moss [96, 1929], Yule and Wilson [153, 1931], Storey, Provine, and Bennett [134, 1929], and others. Wagner and Hyman found that ordinary fatty acids produced by oxidation had little effect on the course of oxidation, and so they concluded that the peracids derived from the initially formed organic peroxides were oxidants, especially when they found that ammonia acted as a strong inhibitor. Peroxide formation during liquid-phase hydrocarbon oxidation has been studied by Chavanne and Bode [40, 1930], who were able to concentrate the organic peroxides and their autoxidation products.

According to Martin, Gruse and Lowy [99, 1933] conjugated diolefines present in cracked spirits oxidize in air to form peroxides, and these act as oxidants.

The large fall in knock-rating of an oxidized cracked spirit which contains organic peroxides is explained by the fact that organic peroxides have a remarkable action in promoting engine knock. Thus, Callendar and colleagues [32, 1927] found that acetone peroxide and ethyl hydrogen peroxide induced violent knocking in the petrol engine. Egerton [55, 1934] reports that diethyl peroxide is rather more potent than amyl nitrite at the same concentration, and its knocking action was inhibited by lead tetraethyl.

Mardles and Moss, also Manning, have reported that the knock-rating of a deteriorated fuel spirit can be raised by washing with a little alkali to remove the accumulated organic peroxides.

An interesting use has been made of the knowledge that organic peroxides are a potent factor in the deterioration of oils by Greenbank and Holm [70, 1934], who express the effect of anti-oxidants in terms of the accumulation of peroxides. They employ the term 'protective factor' of an anti-oxidant and define it as being the ratio of the amount of peroxides in the untreated oil to that in the treated oil. They found maleic acid to give a P.F. of 3·0 compared with 1·3 for fumaric acid.

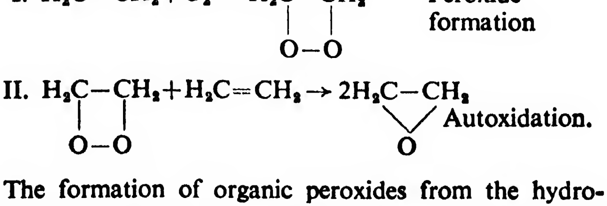
Peroxides and Autoxidation. Accurate knowledge concerning the chemical changes in which organic peroxides are formed from petroleum hydrocarbons and the precise way in which they accelerate combustion is yet to be obtained, but, in general, it is considered that they function as 'oxygen carriers' in the process of autoxidation, that is to say, oxidation of the hydrocarbon molecule proceeds not directly with the relatively inert oxygen molecule but with the reactive peroxide formed previously from another hydrocarbon molecule.

The theory of autoxidation has been fully discussed by Engler [61, 1904]; by Bach [4, 1897]; by Staudinger [131, 1925]; by Moureu and others. In general, the reactions involved are as follows:

I. $A+O_2 \rightarrow AO_2$ peroxide formation.

II. AO_2(autoxidator) + B(acceptor) → AO + BO autoxidation.

Bäckström [5, 1927], in considering the chain reaction theory of negative catalysis, concluded that autoxidation reactions are involved and these occur in two steps, the first oxidation product being a peroxide which then reacts with another molecule of the substance forming the final reaction product. The relative rates of the two reactions vary from case to case. If the second step proceeds relatively slowly, then the peroxide accumulates in the liquid during the course of the oxidation. A similar conclusion has been reached by Milas [102, 1932], who postulated a preliminary addition of oxygen with the subsequent formation of highly metastable peroxides having high instability and energy content. These peroxides may transfer their excess energy to other molecules and thereby initiate new reaction chains either by reverting to ordinary peroxides or by causing intramolecular rearrangement with subsequent splitting off of hydrogen peroxide or organic peroxides. According to the autoxidation hypothesis, for example, the formation of ethylene oxide during the slow combustion of ethylene may be represented by the interaction of ethylene peroxide with another molecule of ethylene:

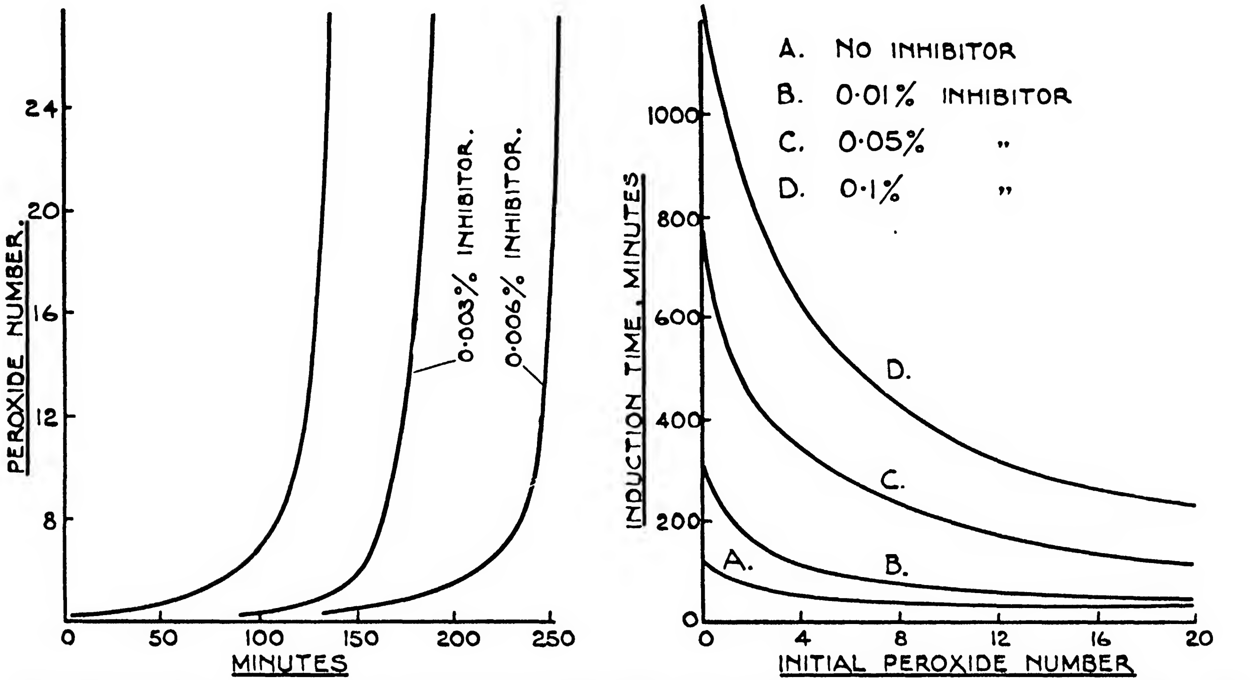


I. $H_2C{=}CH_2+O_2 \rightarrow \underset{O-O}{H_2C-CH_2}$ Peroxide formation

II. $\underset{O-O}{H_2C-CH_2}+H_2C{=}CH_2 \rightarrow 2\underset{O}{H_2C-CH_2}$ Autoxidation.

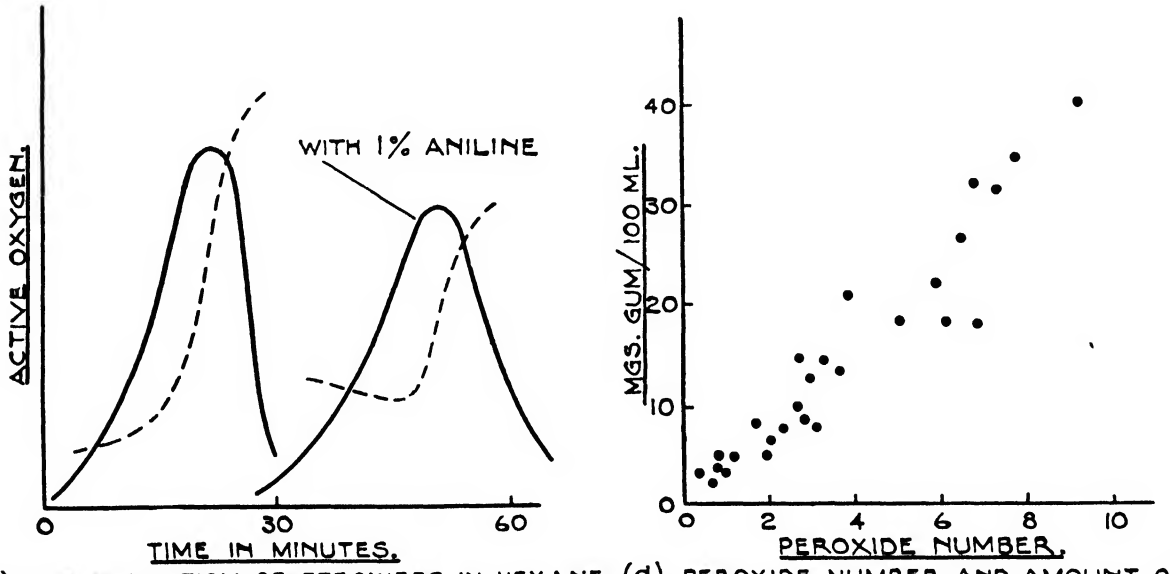
The formation of organic peroxides from the hydrocarbon takes place by the addition of the oxygen molecule to the unsaturated bond which, according to Stephens [132, 1928] and to Lenher [89, 1932] becomes activated in unsaturated hydrocarbons. These peroxides have been isolated and described by Staudinger and others, but in the

FIG. 5. PEROXIDATION DURING HYDROCARBON OXIDATION.



(a) PEROXIDE FORMATION DURING INDUCTION PERIOD OF A CRACKED SPIRIT (MORRELL, DRYER, LOWRY & EGLOFF)[103]

(b.) EFFECT OF PEROXIDE CONTENT ON INDUCTION PERIOD OF A CRACKED SPIRIT (MORRELL, DRYER, LOWRY & EGLOFF.)[103]



(c.) THE FORMATION OF PEROXIDES IN HEXANE-O_2 MIXTURE, WITH AND WITHOUT ANILINE. (BRUNNER)[26]
CHAIN LINE INDICATES PRESSURE RISE.

(d) PEROXIDE NUMBER AND AMOUNT OF GUM FORMED IN CRACKED SPIRIT. (EGLOFF, MORRELL, WIRTH & MURPHY)[56].

FIG. 5.

case of the paraffin hydrocarbons the mode of attack is not so clear. Callendar and Mardles [32, 1928] considered that the oxygen molecule enters between the carbon-carbon linkage, and so forms a dialkyl peroxide, or between the carbon-hydrogen linkage to form a hydrogen alkyl peroxide. Dumanois, Mondain-Monval, and Quanquin [48, 1931] have described engine experiments dealing with the formation and detonation of explosive peroxides in the engine cylinder. They made reference to their earlier investigation [48*a*, 1930] in which they reported identification of alkyl hydrogen peroxides amongst the oxidation products of hydrocarbons. Chavanne [39, 1931] considers peroxidation in the CH grouping with its mobile hydrogen to be the natural course of combustion. Grün [71, 1920] considers the possibility of the oxygen molecule joining at a nascent ethylene linkage, whilst Berl [10, 1928] considers that the paraffin hydrocarbon first loses some of its hydrogen, and oxygen combines with the unsaturated hydrocarbon formed to produce the peroxide. Stephens [133, 1933] has applied a vibrational activation theory to the primary addition of oxygen to a linkage activated by thermal means. Bone [16, 1932] disputes the primary formation of peroxides, and considers that combustion is a process of hydroxylation, peroxide formation being incidental to the oxidation of aldehydes.

Autoxidation by organic peroxides is considered by many workers undoubtedly to occur during the oxidation and combustion of hydrocarbons, both in the liquid and gas phases; if the amount of the peroxide in the mixture is diminished by the addition of a substance, then the rate of oxidation falls in proportion and the substance can be called an anti-oxidant (cf. Article 1). When aniline or benzene is added to a hydrocarbon undergoing oxidation, the benzene becomes autoxidized to phenol and the aniline to a tar, and this can occur at a temperature when both the benzene and aniline remain practically unattacked by oxygen under normal conditions, each being taken singly [93, 1928]. The aniline and benzene are apparently autoxidized by the hydrocarbon peroxides, since it was found that there was a big decrease in peroxide concentration whilst the rate of reaction diminished.

Moureu and Dufraisse likewise consider from the results of many experiments that the organic peroxide primarily formed is the oxidant and that the anti-oxidants act by destroying or reducing the amount of the oxidant. In the case of organo-metallic compounds such as lead tetraethyl, the anti-oxidant decomposes during the combustion in an engine and the lead peroxide momentarily formed from the lead tetraethyl reacts with the fuel organic peroxides and decomposes them. This theory of antagonistic peroxides can be expressed in the following way:

Where A represents a hydrocarbon molecule and B the anti-oxidant,

$A+O_2 \rightarrow A(O_2)$ (the fuel peroxide which acts as oxidant)

$A(O_2)+B \rightarrow AO+BO$ (inert oxidation products)

and/or $A(O_2)+B(O_2) \rightarrow A+B+2O_2$.

Callendar [32, 1927], Egerton [52, 1927], Moureu [107, 1927], and Dumanois [47, 1928] have set forth their explanations on the mechanism of suppression of engine knock by small amounts of lead tetraethyl on the above lines of organic peroxide formation, the thermal decomposition products of lead tetraethyl, namely, lead or lead oxide decomposing the peroxides and so removing the oxidant from the sphere of action.

Experiments by Egerton, by Berl, by Mardles, and by other workers have shown that metals behave similarly to the organo-metallic compounds, whilst Egerton [54, 1931] has shown by several experiments that the metals behave as anti-oxidants only when in an incipient state of oxidation.

From the author's experiments on the slow combustion of hexane with oxidation times of a few seconds, it was found that the presence of various oxides in the ordinary state had little or no effect on the general oxidation behaviour. They were also ineffective in the engine. Layng and Youker [86, 1928], however, using the bulb method of oxidation, found that the oxides of lead could exert an inhibitory action on the oxidation of petrol vapour above 220° C. It appears that the metal itself when in a state of incipient oxidation is the effective part of the organometallic dope (cf. Article 1, p. 2911).

Activation and Chain Reaction. From a consideration of the slowness of reaction during the induction period, it would appear that the normal reaction between hydrocarbon molecules and oxygen molecules occurs with exceptional slowness, and only when an oxidant is introduced in the system or is produced by oxidation in the course of time does the reaction accelerate. The reaction is also speeded up by temperature rise, light, radiation, silent electric discharge, &c., whereby either some of the molecules which have absorbed energy enter into an excited or activated state and become reactive, or radicals are formed which can propagate reaction. It will be realized that not all the molecules in a hydrocarbon-oxygen mixture are capable of reacting, otherwise the reaction would be practically instantaneous; the rate of oxidation at any moment depends upon the concentration of reactive or activated molecules. Arrhenius [2, 1889] considered the thermal activation of molecules, and in his well-known equation for the variation of reaction velocity with temperature,

$$\frac{d\log k}{dT} = \frac{E}{RT^2},$$

where k is the velocity, the quantity E has the dimensions of energy and can be regarded as the heat absorbed in the formation of an active molecule at the expense of a normal one, and for this reason is called the heat of activation. The study of photochemical reactions has shown that not only is one molecule activated by each quantum of light absorbed according to the Einstein law of photochemical equivalence, but sometimes 50,000, and this has been explained by the chain reaction theory [5, 1927; 42, 1928; 78, 1933].

The idea of chain reactions already discussed in Articles 1 and 2 has been introduced into the study of oxidants and anti-oxidants, and from this standpoint an oxidant is defined as a substance which activates a chain of molecules rendering them reactive, and an anti-oxidant is one which breaks the chain or deactivates. With regard to the anti-knock action of iron carbonyl, lead tetraethyl, &c., in the engine cylinder, it can be considered that the oxidants, formed in the combustion mixture by incipient oxidation, are deactivated by the decomposition products of the metal compound. Staudinger uses the term 'moloxide' for the activated primarily formed peroxide in distinction to the isolable peroxides less rich in energy. Theories of anti-oxygen have been made on these lines, namely, that anti-oxidants by reacting with the oxidant, for example, the activated oxygen molecule or the activated organic peroxides formed in the initial stages of combustion, removes it from the sphere of influence. Egerton assuming an 'energy chain' mechanism has expressed the formation of activated molecules in the case of ethane oxidation in the following way:

$$CH_3.CH_3+O_2 \rightarrow CH_3.CH_3O_2{}^* \rightarrow CH_3CHO+H_2O^*$$
$$H_2O^*+O_2 \rightarrow O_2{}^*+H_2O$$

(the star denotes an activated molecule)

here the energy of the peroxide is passed on to the oxygen molecule through a molecule of water.

Thompson and Hinshelwood [139, 1929], who have studied the mechanism of the oxidation of ethylene, consider their experimental results indicate that ethylene first forms an unstable peroxide which sets up chains of reactions throughout the gaseous system. Other examples of activation and chain reaction mechanism in hydrocarbon oxidation are given by Edgar and colleagues [115, 1929] (octanes), Lenher [89, 1932] (ethylene and propylene), and Fort and Hinshelwood [63, 1930] (benzene); Frear [65, 1934]; and Austin Taylor and Riblett [3, 1931].

It will be seen that the autoxidation and chain-reaction theories of the mode of action of anti-oxidants and oxidants in the above hydrocarbon oxidations are not antagonistic but complementary. One is based on concepts of organic chemistry and the other, which is derived from ideas of molecular physics, is independent of the manner in which the chemical change occurs.

Taylor [137, 1923] and later Perrin [113, 1927], then Dupont [49, 1930], have put forward the idea that anti-oxidants combine temporarily with activated molecules of the oxidant, the molecular complex subsequently dissociating with the liberation of inactive molecules. Moureu [106, 1928], in discussing this hypothesis, thinks it unlikely that such a varied assortment of anti-oxidant substances as dissimilar as sodium iodide, hydroquinone, thio-hydracrylic acid, and so on, should all act in the same way. A hypothesis based on the inactivation of oxygen, he considers, is much more possible, since oxygen is a common factor in each case. From the results of their experiments with hydroquinone, Moureu and colleagues prefer the hypothesis involving autoxidation by the initially formed peroxides, rather than the one of inactivation which they consider is quite insufficient to account for the observed anti-oxidant effect. Dhar [44, 1928] favours the autoxidation hypothesis of anti-oxidants and oxidants in preference to one based on chain reactions alone. In thermal oxidations, he considers the anti-oxidant becomes oxidized whilst in action and hydroquinone is no exception.

Egloff and colleagues, in considering the mode of action of anti-oxidants in cracked spirits, point out that there is a close relationship between the critical oxidation potential (index to ease of oxidation) of the anti-oxidants and their inhibitory action. The superiority of ortho- or para-substituted compounds over their meta isomers—seen in comparing resorcinol and catechol, or in the cresols and xylenols—is linked with the effect of ortho- or para-substitution on oxidation potential. Similarly, the superiority of alpha- over beta-naphthol is related to the lower potential of the former compound.

A good deal of further investigation must be carried out before the precise modes of action of various anti-oxidants in rendering the oxidant ineffective are elucidated. Undoubtedly an explanation of anti-oxidants and oxidants as applying to hydrocarbons involves both the concepts of autoxidation and of activation and chain mechanism of reaction.

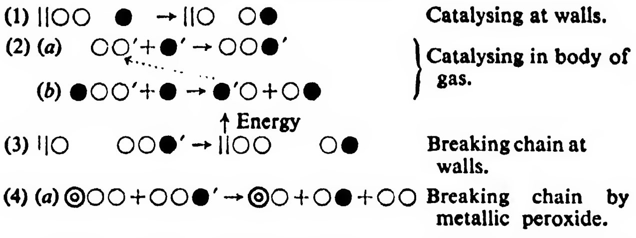
Interesting information relating to the theory of catalytic and anticatalytic action of small traces of foreign substances was given in the reports of the discussion on homogeneous catalysis by the Faraday Society, 1928.

Chemi-luminescence. One of the first manifestations of chemical change in many combustible gaseous mixtures on heating is a faint luminous glow or luminescence which, unlike a true flame, does not possess sharp boundaries but extends in the form of a cloud throughout the heated gas mixture. Anti-oxidants extinguish the glow, so there is an interesting comparison between the extinction of luminescence by inhibitors and the action of lead tetraethyl in raising the self-ignition temperature of ignitible gases; in both cases there is an initial suppression of chemical change, indicating the similarity of the mechanism of inhibition. Gill, Mardles, and Tett [68, 1928] have studied the action of oxidants and anti-oxidants on the luminescence of hexane-air mixtures. A 13·7% mixture of normal hexane in air began to show luminescence and fog formation at 308°, followed by intermittent glow pulses and rapid thickening of the fog at 315°. The bluish glow as it passed the thermo-couple raised the temperature to 340° momentarily. Nitrogen peroxide caused fog to appear at a temperature 50° below the fog temperature of hexane-air alone. It completely prevented the appearance of intermittent luminescence and continuous glow, but the mixture exploded violently at 430° C. Ethyl nitrate and carbon disulphide had no effect on the glow; carbon monoxide appeared to brighten it, whilst ammonia and the vapour of bromine, ethyl alcohol, and methyl alcohol extinguished it. The effect of a little lead tetraethyl vapour on the mixture was to delay the glow from 305° to 350° and to make the combustion wave much cooler.

Aniline vapour (1%) was found by Coffey and Birchall [43, 1934] to cause the lower bluish flame zone in hydrocarbon combustion to disappear entirely and to increase the upper self-ignition temperature by over 20°, whilst nitrosobenzene was found to decrease the self-ignition temperature.

The hexane glow observed by Gill, Mardles, and Tett appeared to be quite unaffected by platinum, gold, silver, copper, aluminium, and tin foils. Thallium, chromium, lead, and vanadium pentoxide had also little or no effect: the only apparent effect of an iron strip was to cause the glow to spread over the surface of the iron, the intensity remaining unchanged. However, the metal surfaces were known to increase the oxidation rate.

Effect of Surfaces. It is necessary to include some reference to the action of surfaces on hydrocarbon oxidation and combustion, because the phenomena of surface oxidation (heterogeneous reactions) can be explained to some extent in terms of activation, deactivation, and chain reaction; the effect of lead tetraethyl in the gas phase can be imitated by using metallic lead and that of iron carbonyl by metallic iron, indicating that the organic metallic compound is effective by providing a deactivating surface of metal or metal oxide. It has been found by Mardles and by Egerton that metal surfaces decrease the amount of detectable peroxides; presumably the surface destroys them in some way and so tends to raise the igniting temperature. In most hydrocarbon oxidations, even in a glass or silica vessel, the walls play some part, and this effect can be studied by packing the vessel with glass beads or powdered silica. With regard to the influence of surfaces on combustion by catalysis or by breaking chains, Egerton has put forward the following scheme in order to indicate broadly that, although results were different, the fundamental happenings were similar (double line signifies metal; black, fuel; white, oxygen; dash, activation):



Pease [112, 1929] found from his study of the characteristics of the non-explosive oxidation of propane and butane that glass packing suppressed the reaction, especially if the surface was coated with potassium chloride.

Bone [15, 1933] has summarized his work on surface combustion by stating (1) that the power of accelerating gaseous combustion is possessed by all surfaces at temperatures below the ignition point in varying degrees, dependent on their chemical character and physical texture; (2) that such accelerated surface combustion is dependent on a prior adsorption of the combustible gas, and probably also of the oxygen by the surface, whereby it becomes 'activated' by association with the surface; (3) that the rate at which the so-'activated' combustible gas is burned is relatively very great compared with the rate at which it is rendered active, so that the controlling factor in the process is not the actual rate of combustion at the surface, but the rate of 'activation' of the combustible gas, which is, in turn, proportional to its pressure; and (4) that the surface itself becomes electrically charged during the process.

From Fig. 2 it will be seen that the metal surfaces not only alter the temperature of initial oxidation but also have a profound effect on the temperature coefficient; chemical analyses of the gases at different temperatures and stages of oxidation show that the presence of iron and lead tend to decrease the amounts of aldehydes, acids, organic peroxides, and other intermediate products, whilst increasing the amount of water and carbon dioxide. It would appear that the metal surface does not necessarily prevent the formation of intermediate oxidation products but tends to crowd them together and hasten their further oxidation to the final products. The function of a metal or organometallic compound in promoting the formation of water and carbon dioxide yet inhibiting peroxides which tend to promote engine-knock is of significance in relation to the fact that in the engine cylinder the presence of lead tetraethyl, whilst suppressing knocking, does not slow up the ordinary combustion.

From the experiments of Carr and Brown [36, 1929] on the rate of pressure rise during gaseous explosions, the effect of lead tetraethyl appeared to be governed by the rate of combustion of the explosive mixture. As the rate of reaction (or rise in pressure) increased, the retarding action of the lead tetraethyl disappeared and was even replaced by an accelerating action on the combustion. The phenomenon was explained on the grounds that the decomposition products of lead tetraethyl are the actual anti-oxidants, so if in the region ahead of the flame the rate of decomposition of lead tetraethyl is less than the rate of inflammation the anti-oxidant effect is not obtained. The main function of lead tetraethyl in the engine cylinder appears to be the suppression of oxidation changes leading to violent ignition of the unburnt charge ahead of the flame (cf. Article 1).

Experimental data regarding the combustion of hydrocarbons in the vapour phase in the presence of organometallic compounds which decompose to form a cloud of metal and metal oxide dust are contained in the literature, and the following selection shows that anti-knocks act as anti-oxidants.

Callendar and colleagues [32, 1927] found that, in the oxidation of normal hexane in air passed through a glass tube, the addition of a little iron carbonyl or lead tetraethyl vapour suppressed the oxidation rate at 500° more than tenfold. Mardles [93, 1928] found a similar anti-oxidant effect using a closed bulb method. Berl [10, 1928] confirmed this anti-oxidant effect; at 400° C. with 0·1% carbonyl present in a hexane-air mixture, the amount of water formed during the oxidation was reduced from 10 to 3% and the residual oxygen in the mixture increased from 1 to 8·9%. With 1% iron carbonyl present, even at 700° the amount of water and aldehydes was less than that formed at 400° with the plain hexane-air mixture. Lead tetraethyl (to 1%) and aniline (to 20%) behaved similarly to iron carbonyl in suppressing oxidation in air at 400°, both with hexane and cyclohexane (cf. Article 1).

Pope, Dykstra, and Edgar [115, 1929] have carried out experiments with isomeric octanes to determine the effect of lead tetraethyl on the oxidation rates. They also concluded from the results that there is a close relationship between the phenomena of knock suppression and the suppression of oxidation reactions.

Pro-knocks and Anti-knocks.

It is generally agreed that anti-knocks act in the capacity of anti-oxidants, the oxidation changes in the fuel charge ahead of the flame being suppressed or delayed [101, 1923]. A large number of substances have been tried out in the petrol engine by various workers with a view to finding suitable anti-knock fuels and to discovering the cause of engine knock.

Small amounts of organic peroxides, ozone, amyl nitrite, ethyl nitrate, or nitrogen peroxide, promote severe knocking whilst, on the other hand, corresponding amounts of lead tetraethyl, iron carbonyl, or nickel carbonyl delay knocking. Many other substances must be added in much larger quantity before their effect is felt, such as ethyl ether, nitrobenzene, normal heptane, &c., which tend to reduce the knock rating and benzene, aniline, phenol, &c., which tend to raise it. Charch, Mack, and Boord (1926) studied the effect of various compounds of lead and other metals as anti-knocks. Some of their engine results, expressed in terms of the efficacy of lead tetraethyl taken as 100, are given in Table II.

Many lead compounds were found to be without effect, including the following: benzaldehyde lead, lead tetrastearate, lead tetracetate, lead diphenyl carbazide, &c. Numerous other metallic derivatives were also found to be without effect; these included sodium zinc ethyl, gold chloride, ferric dimethyl glyoxime, aluminium diethyl, dicarbonyl chloroplatinite, nickel dimethyl glyoxime, copper diphenyl carbazide, cobalt succinimide, chromium pentaphenyl bromide, and nitrogen sulphide.

Boyd [19, 1924] in his investigations found that nitrogen exerts a greater influence upon the character of combustion than any other element of small atomic number. Those nitrogen compounds which tended to suppress knocking were the primary and secondary amines, particularly those containing an aryl group. Some of his results are given in Table III.

TABLE II

Anti-knock Compounds

Compound	*Formula*	*Anti-knock Coefficient*
Lead tetraethyl	$Pb(C_2H_5)_4$	100
Lead tetraphenyl	$Pb(C_6H_5)_4$	59
Lead diethyl dichloride	$Pb(C_2H_5)_2Cl_2$	67
Lead diphenyl dimethyl	$Pb(C_6H_5)_2(CH_3)_2$	97
Lead diphenyl di-iodide	$Pb(C_6H_5)_2I_2$	80
Lead ethyl xanthogenate	$Pb(C_2H_5OCSS)_2$	7·1
Bismuth triphenyl	$Bi(C_6H_5)_3$	18·2
Bismuth trimethyl	$Bi(CH_3)_3$	20·2
Stannic iodide	SnI_4	12·8
Tin diethyl di-iodide	$Sn(C_2H_5)_2I_2$	12·3
Cadmium dimethyl	$Cd(CH_3)_2$	1·05
Triphenyl arsine	$As(C_6H_5)_3$	1·4 (approx.)
Aluminium ethyl iodide	$Al_2(C_2H_5)_3I_3$	very weak (due to iodine content)

TABLE III

Effects on the Anti-knock Value of Aniline of Substituting Various Organic Radicals for Hydrogen in the Ring and in the Amine Group

Compound	*Formula*	*Reciprocal of mols. required to give anti-knock effect equivalent to 1 mol. of aniline*[1]
Aniline	$C_6H_5NH_2$	1·0
Toluidine	$CH_3C_6H_4NH_2$	1·22[2]
m-Xylidine	$(CH_3)_2C_6H_3NH_2$	1·4
Cumidine	$(CH_3)_3C_6H_2NH_2$	1·51
Ethylaminobenzene	$C_2H_5C_6H_4NH_2$	1·14
Amylaminobenzene	$C_5H_{11}C_6H_4NH_2$	1·15
Monomethylaniline	$C_6H_5NHCH_3$	1·4
Mono-*n*-propylaniline	$C_6H_5NHC_3H_7$	0·75
Diphenylamine	$C_6H_5NHC_6H_5$	1·5
Dimethylaniline	$C_6H_5N(CH_3)_2$	0·21

[1] Based on concentrations of aniline up to 3% by volume in kerosine.

[2] Average of *o*, *m*, and *p* values.

The effects of nitrogen compounds are small in comparison with those of other elements; Boyd gives the following table to illustrate this:

TABLE IV

Nitrogen compared with some other elements in effect upon combustion

Element	*Compound*	*Reciprocal of mols. required to give an anti-knock effect equivalent to 1 mol. of aniline*
Nitrogen	$(C_2H_5)_3N$	0·14
	$(C_6H_5)_2NH$	1·5
Selenium	$(C_2H_5)_2Se$	6·9
Tellurium	$(C_2H_5)_2Te$	26·8
Lead	$(C_2H_5)_4Pb$	120·0

In addition to the organo-metallic derivatives of lead and the carbonyls of iron and nickel, other metallic compounds have been claimed for use as anti-knocks. Compounds of thallium, cobalt, chromium, vanadium, &c., and potassium salts [5, 1927] and potassium gallate [60, 1928], have been proposed for the purpose of raising the knock rating of fuels. Copper or ferric compounds of oxymethylene camphor and the copper compound of amino-methylene-acetone or of oxymethylene-acetophenone in motor fuels are claimed in B.P. 370,287 (7 April 1932); copper dispersed in methyl cyclohexanol is claimed in B.P. 267,079.

The great disadvantage of using metallic compounds dispersed or dissolved in gasoline is the trouble of deposits in the engine. Lead tetraethyl is used in the form of ethyl fluid of the following composition (Banks):

Lead tetraethyl	61·4% by weight.
Ethylene dibromide	35·7% „
Dye	0·2% „
Kerosine, &c.	balance
Sp. gr. at 20° C.	1·755

(proportion of lead tetraethyl in fluid by volume is 65·5%).

The inclusion of ethylene dibromide was the result of extensive investigation. This halogen bearer converts the lead oxide to lead bromide which is volatile at the working temperatures prevailing in the cylinder and is evacuated along with the exhaust gases.

The maximum concentration of lead tetraethyl generally used in any fuel, for commercial purposes, is 3·6 c.c. per imperial gallon, but for government and military purposes the concentration is sometimes increased to 7·0 c.c. per imperial gallon. It has been found that some gasolines respond more to the effect of lead tetraethyl than others [75, 1932; 7, 1934]; thus a gasoline from a California oil had a highest useful compression ratio (H.U.C.R.) of 5·4, one from a Burma petroleum an H.U.C.R. of 5·6, yet the addition of 0·7 c.c. of lead tetraethyl brought both gasolines to an H.U.C.R. of 5·8. The use of iron carbonyl as an anti-knock in the fuel known as 'Motalin' appears to have been discontinued since 1929 (cf. Article 11).

Alcohols, benzene, toluene, cracked spirit, or casing-head spirit may be used for increasing the knock rating of a straight run gasoline, but the addition of some substances, such as, for example, butyl alcohol, aniline, tetralin, phenol, &c., which must be added in fair quantity before their anti-knock effect is felt, interferes with the volatility of the fuel and sometimes enhances the difficulties of corrosion and the deterioration during storage, also the fouling of the engine. Information relating to the knock rating of a large number of hydrocarbons, alcohols, amines, &c., either alone or in blends, is given by Garner, Evans, Sprake, and Broom [67, 1934], by Schmidt [125, 1934], and by Lovell, Campbell, Signaigo, and Boyd [91, 1934] (cf. Article 10).

Oxidants and Anti-Oxidants in Cracked Spirits.

The modern development of 'cracking' petroleum residual oils with a view to obtaining increased yields of motor spirit of a high knock rating has introduced the problem of stabilizing these fuels against deterioration by oxidation during storage. In addition to the paraffin and ring hydrocarbons normally in straight-run gasolines, cracked spirits contain unsaturated hydrocarbons which, by a complex process of oxidation and polymerization, form gums and acids with a corresponding fall in knock rating during storage. If it were possible to prevent aeration of the cracked spirits from the time of distillation to the time of use, apparently little or no change in the spirit would be expected; but since during some stage of its history the fuel inevitably comes in contact with air, there is always a possibility that gumming and a fall in knock rating might occur during storage, even with well-refined spirits containing only a small proportion of olefines. Attempts to remedy this defect have been made from two main standpoints, (*a*) by careful refinement to remove the readily oxidizable diolefines and sulphur compounds, and (*b*) by the use of anti-oxidants which delay the initial peroxide formation. During the refining process there is usually a considerable loss of valuable olefine hydrocarbons and so, to avoid excessive losses by elaborate refining, use is made of a wide range of anti-oxidants.

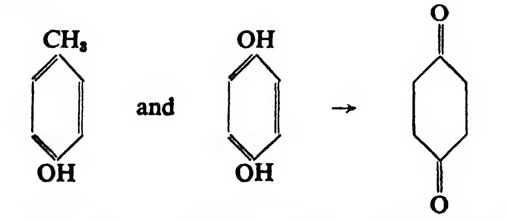
It has been found that in the liquid-phase oxidation of hydrocarbons the substances which are most capable of inhibiting oxidation are of the phenolic class; for example, hydroquinone, phenol, cresols, thymol, pyrogallol, &c., and of the amino or organic derivatives of ammonia class; for example, para-amino-phenol, beta-naphthylamine, urethane, &c. Many of these phenolic and amino substances give prolonged storage life to a fuel spirit, but considerable discretion is needed in their selection and in the amount to be used, because under some conditions they are liable to augment the difficulties by causing discoloration or deposits and, in extreme cases, even of behaving as accelerators, after ageing. The aromatic amines, e.g. aniline, toluidines, diphenylamine, &c., in particular, must be used with considerable care, because they themselves become oxidized eventually to gummy substances and so contribute to the gumming difficulties. Egloff and co-workers [59, 1932] have shown, with a Pennsylvanian cracked spirit by their method of test using an oxygen bomb, that the aromatic diamines were more potent than the mono-amines in prolonging the induction period. Phenyl alpha-naphthylamine and para-amino dimethyl aniline were very effective. *p,p*-Diaminodiphenylamine (0·01 %) inhibited deterioration in the spirit tested over a period of 6 months and was shown to be a good inhibitor by the bomb test. The effectiveness of the aromatic amines, however, varies considerably from spirit to spirit.

Better results appear to be obtained when the amino group is modified by forming an acyl derivative such as in acetanilide, or when a carboxyl group is adjacent to the amino group such as in glycine or oxamine.

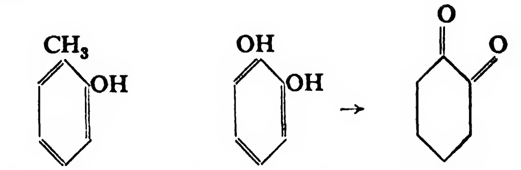
Tricresol, which is the name given to the coal tar phenolic fraction boiling 195–203° C., has been found to give satisfactory results, when present in the optimum amount of 0·03 %, in stabilizing benzoles for fuel purposes, and it is considered that the stabilized benzoles are little inferior to those purified by acid wash [80, 1926–30].

The ortho- and para-cresols surpass meta-cresol in anti-oxidant action, and this is believed to be due to the capacity of the former substances to form quinones by oxidation.

Moureu and Dufraisse in their initial researches found that hydroquinone, pyrocatechol, and pyrogallol possessed far greater anti-oxidant properties than did phenol and resorcinol.



para-cresol hydroquinone para-quinone



ortho-cresol pyrocatechol ortho-quinone

Similarly, it has since been found that hydroxy-hydroquinone and pyrogallol are more effective than phloroglucinol, presumably for the same reason that they more readily form quinone.

Rogers and Voorhees [120, 1933] found 4, 4 dihydroxydiphenyl to possess considerable anti-oxidant activity, and this they suggest is possibly due to its oxidation to diquinone.

The anti-oxidants suitable for cracked spirits are not necessarily confined to compounds containing a phenolic and amino group; a large number of substances outside these classes have been reported on or disclosed in patent literature as giving beneficial results. Some of these are included in the following list (Table V):

TABLE V

Substance	*Reference*
Seleno mercaptans (phenyl or ethyl seleno mercaptans)	Rosenstein, L., and Hund, W., U.S.P. 1,835,184 (1931). [121].
Acyl derivations of an aromatic amine (acetanilide)	Calcott and Lee, U.S.P. 1,789,302. (1931). [31].
Imidines (phthalimidine)	Jaeger. U.S.P. 1,908,705 (1933). [81].
Phthalide (hexahydrophthalide)	Jaeger. U.S.P. 1,914,509. [81].
Piperazine	Mardles, *Proc. World Petr. Congress*, 1933. [95].
Nicotine	,, ,, ,, ,,
Hexamine	,, ,, ,, ,,
Ammonia	Wagner and Hyman, *J.I.P.T.* **15**, 674. (1929). [143].
1, 2 naphthoquinone	Egloff, Morrell, Lowry, and Dryer. *J. Ind. Eng. Chem.* **24**, no. 12, 1375 (1932). [59].
Quinhydrone	,, ,, ,, ,,
Phenoxazine	,, ,, ,, ,,
Naphthalene 0·1%	Egloff, Faragher, and Morrell. *Oil and Gas J.* **28** (29), 116 (1929). [57].
Anthracene 0·1%	,, ,, ,,
Pyrene	,, ,, ,,
Phthalic anhydride	,, ,, ,,
Organic compound containing the group =N·N= (4, 4 diphenyl semi-carbazide)	Burke. Can. P. 339,715 (1934). [28].
Gum camphor	Sullivan. *Oil and Gas J.* **29** (42), 156 (1931). [135].
Camphor, camphorphorone camphoric acid	J. Morrell. U.S.P. 1,930,248 (1933).
Nitro compounds	Somerville. B.P. 289,347 (1926). [128]. Hoffert and Claxton, 1933. [79].
Oxalic acid	Std. Oil Co. B.P. 348,011 (1929). [130].
Stannous oleate	,, ,, ,,
Stannous chloride	,, ,, ,,
Sodium methylate	,, ,, ,,
Sodium iodide	Moureu, Dufraisse, and Chaux, *Compt. rend.* **184**, 413 (1927). [106].
Arsenic tri-iodide	,, ,, ,,
Malachite green dye	,, ,, ,,
Peri-monoxy naphthalene	B.P. 399,733.

Since it is important to select the most suitable and the correct amount of an anti-oxidant for any particular fuel spirit, it is necessary to carry out accelerated storage tests in order to obtain some idea of the amount of gum likely to be formed (potential gum) during an interval of time. All the methods proposed for potential gum determination are based on oxidation; a complete summary of these is given in the *Proceedings of the World Petroleum Congress*, 1933, Vol. 2, p. 85, by Egloff and colleagues.

The accelerated oxygen bomb test (Aldrich and Robie [1, 1932]; Bridgeman [20, 1932]; Egloff, Morrell, Lowry, and Dryer [56, 1933]; Ramsey [118, 1932]; Ward [144, 1932]; and Winning and Thomas [149, 1933] has been used to a considerable extent and is useful in a refinery for obtaining information quickly regarding the probable storage life; precise correlation, however, between actual storage results and the length of the induction period has not always been obtained (Bridgeman [20, 1932]; Bespolov and Degtyareva [11, 1932]; Sullivan [135, 1931]; Winning and Thomas [149, 1933]; Flood, Hladky, and Edgar [62, 1934]), and in the opinion of Mardles and Moss [97, 1933] severe oxidation conditions in any potential gum test are to be avoided, especially when anti-oxidants are present, these being so sensitive to conditions. Mardles [95, 1933] found that some substances decreased in anti-oxidant action with rise of temperature or even inverted to oxidants and so, in a search for suitable substances as anti-oxidants, a mild incubation test in air, as near as possible to the actual storage conditions, is recommended.

Egloff and colleagues, using a Pennsylvania cracked spirit with a normal induction period in the bomb of 45 minutes, obtained the following results, using 0·01% by weight of various organic substances:

TABLE VI

(a) Phenolic Compounds

	Induction period (min.)
Monohydroxy	
Phenol	75
o-Cresol	135
m-Cresol	75
p-Cresol	210
Tricresol (tech.)	135
Butylphenol (para and ortho mixed)	195
tert-Butylphenol (para and ortho mixed)	210
4-Hydroxyl-1: 3-dimethylbenzene	420
2-Hydroxy-1: 3-dimethylbenzene	420
4-Hydroxy-1: 2-dimethylbenzene	255
2-Hydroxy-1: 4-dimethylbenzene	285
Thymol	300
Carvacrol	180
Polyhydroxy	
Catechol	2,400
Resorcinol	150
Orcinol	150
4-Butylresorcinol	360
4-Hexylresorcinol	390
4-Heptylresorcinol	300
Hydroquinone	85
Toluhydroquinone	70
Pyrogallol	2,185
Phloroglucinol	90
Polycyclic	
alpha-Naphthol	2,250
beta-Naphthol	330
1:5-Dihydroxynaphthalene	1,705
o-Hydroxydiphenyl	60
p-Hydroxydiphenyl	135
Nitroso-naphthol	135

(b) Amines

Aromatic monoamines	
Aniline	45
o-Toluidine	60
Diphenylamine	105
Polyamino compounds	
o-Phenylenediamine	450
m-Phenylenediamine	165
p-Phenylenediamine	960
m-Toluylenediamine	240
p-Aminodimethylaniline	635
p-Aminodiethylaniline	375
p-*p*-Diaminodiphenylamine	945
Benzidine (0·05%)	195
o-Tolidine	120
2: 4-Diaminodiphenylamine	880
Naphthyl amines	
α-Naphthylamine	105
β-Naphthylamine	75
Ethyl-α-naphthylamine	165
Phenyl-α-naphthylamine	720
Phenyl-β-naphthylamine	195

(c) Aldehyde-amine Condensation Products

Acetone-aniline	420
Acetone-diphenylamine	330

(d) Amino and Nitrophenols

o-Aminophenol	1,320
m-Aminophenol	330
p-Aminophenol	2,340
2-Amino-5-hydroxytoluene	1,785
3-Nitro-4-hydroxytoluene	50
2-Amino-4-nitrophenol	1,260

Egloff in discussing his results considers the bomb method to be useful in distinguishing inhibiting substances from those that are not effective, the increase in storage life not being necessarily the same as might be expected from the increase in induction period. Hydroquinone, for example, gave a comparatively short bomb induction period yet it protected a fuel for over 6 months in actual storage.

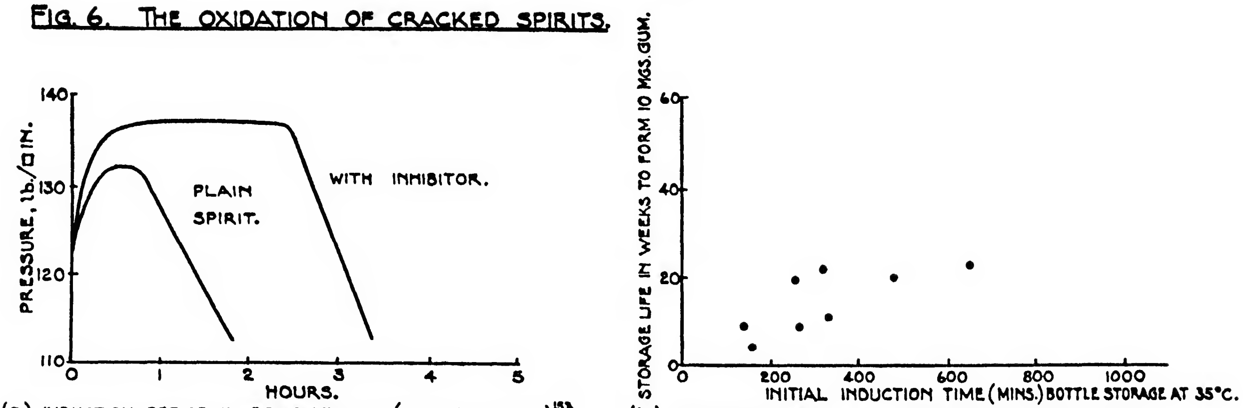
From Fig. 6, it will be seen that there is a rough parallel between storage life and the induction time in numerous instances; also there is a rough relation between the peroxide number and gum formation, Fig. 5, and gum formation with the fall in knock rating.

In addition to the measurement of the induction period in the bomb method, some idea of the storage life of the fuel is given by the amount of gum formed during an arbitrary period of time in the bomb; Scheumann [124, 1933] using this procedure has studied the gum inhibiting action of anti-oxidants from the stand-point of the ratio:

Gum inhibiting index = average potential gum reduction/average concentration of inhibitor mg. per 100 ml.

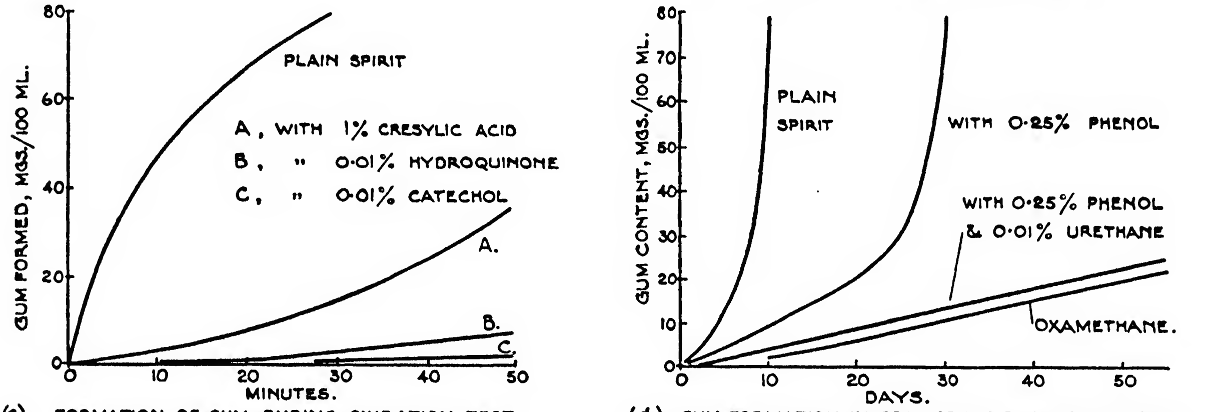
Small amounts of mineral acids appear to have a strong accelerating effect on the deterioration of cracked spirits; even the addition of 0·01 metol (*p*-methylaminophenol sulphate) to a coal spirit accelerated the deterioration, although the free base has an inhibitory action. Wagner and Hyman have published data showing the inhibitory action of ammonia on a cracked spirit. They found that after 52 days' storage the plain spirit had increased in gum by 203 mg., whilst with hydroquinone the gum increase was 42, and with ammonia 35. They suggest the reason of the

FIG. 6. THE OXIDATION OF CRACKED SPIRITS.



(a) INDUCTION PERIOD IN BOMB METHOD (YULE & WILSON)[153].

(b.) RELATION BETWEEN INDUCTION PERIOD AND STORAGE LIFE. (ROGERS, BUSSIES & WARD).[119]



(c) FORMATION OF GUM DURING OXIDATION TEST IN BOMB (THOMAS).[188]

(d.) GUM FORMATION IN COAL SPIRIT DURING STORAGE AT 85°C. (MARDLES).[95]

FIG. 6.

decrease is the reduction of the hydrogen-ion concentration. This view was strengthened by the discovery that a trace of hydrogen chloride gas not only caused polymerization in gum-free vapour phase cracked spirit, but also promoted profound oxidation. Hoffert [79, 1933] reported that traces of mineral acid present in benzoles were sometimes sufficient to spoil the action of cresylic inhibitors. Acetic acid exerted a faint catalysing action. Ammonia under some circumstances increased the gum yield. On the other hand, considerable improvement was obtained with various classes of olefinic fuel spirits using ammonia gas and ammonia derivatives.

Some results with these inhibitors are given in Table VII and Fig. 6.

TABLE VII

Influence of various nitrogen compounds on gumming tendency

(a) Liquid-phase cracked spirit, stored for 1 month at 30° C. in one-fifth filled flasks, in dark

	Gum mg. per 100 ml.
Plain	38
„ +piperazine	42
„ +hexamine	5
„ +urea	8
„ +piperine	35
„ +thio-urea	7
„ +uric acid	15
„ +nicotine	16
compare with	
Plain+hydroquinone	13

(b) Sample of redistilled liquid-phase cracked spirit stored at 35° in one-tenth filled flasks for 3 and 5 days. Additions of solids up to 0·05%; liquids up to 0·25%

	Gum mg. per 100 ml. After 3 days	Gum mg. per 100 ml. After 5 days
Plain	5	14
„ +ammonia	12	14
„ +pyrrol	8	12
„ +formanilide	8	11
„ +carbanilide	5	12
„ +para-aminoacetanilide	6	12
„ +quinoline	5	12
„ +piperazine	3	7
„ +pyridine	5	9
„ +aminoacetic acid	4	5
compare with		
Plain+phenol	—	12

(c) Sample of redistilled coal spirit stored at 30° in one-tenth filled flasks for 8 days

	Gum mg. per 100 ml.
Plain	30
„ +0·05% piperazine	9
„ +0·05% *p*-aminoacetanilide	8
„ +0·2% *p*-aminophenol	25
„ +0·05% aminoacetic acid	18
compare with	
Plain +0·25% cresylic acid	16
„ +0·25% carbolic acid	12
„ +0·02% hydroquinone	4

(d) *Sample of redistilled coal spirit stored at 25° in one-tenth filled bottles in dark.* (*The storage life is equivalent to the time in days taken to reach 20 mg. gum per 100 ml.*)

	Storage life.
Plain	11 days.
„ +0·005% urethane	21 „
„ +0·01% „	19 „
„ +05% „	18 „
„ + 0·01% urethane 0·005% thymol	35 „
„ + 0·005% piperazi 0·005% urethane	30 „
„ + 0·01% oxamethane	16 „
„ + 0·01% oxamethane 0·005% alpha naphthol	35 „

As might be expected from a consideration of the sensitivity of anti-oxidants to change of conditions, the efficacy of a substance varies according to the variety of fuel spirit, method of refinement, conditions of storage, &c., so it appears necessary to try out any likely inhibitor for some particular fuel by a suitable laboratory test; the apparently erratic results given in the literature of fuel anti-oxidants are due, undoubtedly, to the differences in the specific character of the fuels, methods of test, and amounts used by the various investigators. The two main classes of gum inhibitors, namely, the phenols and organic bases, can be used together with advantage, the benefit from the mixed anti-oxidant often being much better than when either are taken singly in the same amount; substances containing both the phenolic and amino groups—for example, para-amino phenol and mono-benzyl-para-aminophenol—are exceptionally efficient as anti-oxidants.

W. H. Thomas [138,1933] has compared 60 compounds of possible value as gum inhibitors with catechol; mono-benzyl-para-amino phenol gave a good comparison, also para-benzylidine aminophenol and para-benzyl aminophenol, but the latter suffered the disability of causing colour development. Colour development was also found with beta-hydroxyphenyl, beta-naphthylamine, di-aniline hydroquinone, dibutylamine, alpha-naphthol, and other inhibitors. W. H. Thomas is of the opinion that it may be necessary to use separate anti-oxidants to prevent the deterioration due to both gum and colour formation.

Oxidants and Anti-Oxidants in Mineral Oils.

Lubrication failures are as often due to deterioration of the oil by oxidation as to any other cause and are not necessarily due to lack of oiliness; oxidation of a mineral oil up to a certain point has often a beneficial action, but when sludging and separation of oxidation products begin with the tendency to emulsification of the oxidized oil rapid deterioration of the oil occurs. It is not surprising, therefore, that much experimental work has been done with anti-oxidants in mineral oils with a view to preventing or minimizing sludging and general oxidation. The conclusions reached with oil anti-oxidants are similar to those in other fields, namely, that there is a wide divergency in efficacy with variations in the kind of oil and with change of conditions. Under severe conditions it is possible for an anti-oxidant to invert and accelerate oxidation and increase sludging by the addition of its own oxidation products to that of the oil.

The deterioration of a mineral oil by oxidation resembles the slow combustion of hexane in air, or the gumming of a cracked spirit during storage, in so far as there is a fairly well-defined induction period during which organic peroxides and other oxidation products tend to accumulate. Brooks [22, 1926], Haslam and Frolich [73, 1927], Yamada [150, 1931–3], and others who have studied the mechanism of the oxidation of mineral oils point out the significance of peroxide formation and, in general, the opinion is held that the oxidation of oils is an auto-catalytic process, the products of reaction being the oxidants for the further rapid oxidation.

Haslam and Frolich investigated the action of anti-oxidants on the oxidation of a sample of highly refined Parke-Davis oil by means of a bubbling method; dry oxygen was bubbled at a rate of 10 litres per hour through 75 g. of the oil at 130° in a glass tube. The development of acidity and rise in viscosity were determined. The results of some of their experiments are shown in Fig. 4, and it will be seen that the action of the various organic substances is to prolong the induction period during which there is no detectable rise in acidity, whilst, on the other hand, iron oxide and copper oxide accelerate the rate of deterioration. They found that phenyl isocyanide, para-toluidine, 1, 2, 3-xylidine, quinoline, and diphenyl decreased the induction period, whilst aniline, tolidine, phenylhydrazine, hydroquinone, and oxanilide were without effect. The reaction when once started always proceeded at the same or similar rate whether the oxidation started at once or had been delayed for a certain length of time by the anti-oxidant. A precisely similar behaviour was observed by Yamaguchi [151, 1930], who studied the anti-oxidant action of diphenylhydrazine, alpha-naphthylamine, hydroquinone, &c., on the oxidation of castor oil.

Yamada and colleagues [150, 1930] in their researches used a manometric method for measuring the oxygen absorption of oils. They paid special attention to the peroxide chemistry of the oxidation changes since they regarded peroxidation as being the primary oxidation change. They found, as other workers have found, that oils, after standing, contained organic peroxides and these oils absorbed oxygen faster than the new oils and were less responsive to anti-oxidants. All the anti-oxidants examined, with the exception of hydroquinone, reduced the peroxides to some extent within a short time.

The following substances were found to inhibit oxidation in an insulating mineral oil:—mercaptans, isoamyl sulphide and other alkyl sulphides, sulphur 0·1% (with 0·2% sulphur the oil formed more sludge than the plain oil), selenium; magnesium, tin, aluminium, and zinc decreased the amount of sludge formed, whilst, on the other hand, the amount was increased by copper, brass, silver, and lead. Lead, zinc, iron, and magnesium tended to reduce the development of acidity. 0·1% tin soaps inhibited sludge formation in a Japanese asphaltic base oil and a similar behaviour was observed with soaps (2%) of calcium, barium, mercury, potassium, and magnesium. Sludging was increased with soaps of copper, iron, manganese, silver, and cobalt. The oxidizibility of a mineral oil was found by Tuichinin and Ivanov [142, 1931] to be increased by the addition of naphthenic salts of potassium, sodium, lithium, iron, and manganese.

Chebotar [41, 1934], working on the oxidation of transformer oils at 150° with oxygen under pressure, found that many of the usual anti-oxidants were without effect or behaved as oxidants although they were effective with paraffin (Nujol). With Nujol he found beta-naphthylamine effective and to a lesser degree beta-naphthol, alpha-naphthylamine, and alpha-naphthol. A beneficial effect was also observed with diphenylamine, oleic acid, and tetraline. 1% beta-naphthylamine increased the induction time from 12 to 180 minutes, and decreased the amount of oxygen absorbed in mg. per 100 ml. from 590 to 8; alpha-naphthol increased the induction time to 100 minutes and decreased the oxygen absorption to 16. On the other hand to transformer oil beta-naphthylamine acted as an oxidant and decreased the induction time from 150 to 100 minutes, having increased the oxygen absorption from 56 to 68.

Interesting information is disclosed in the patent literature dealing with the use of anti-oxidants in oils for the purpose of minimizing sludging. King [83, 1933] found a beneficial effect from the use of lead tetraethyl in mineral oils particularly in minimizing the carbonization of the oil in the combustion space of an engine.

A similar beneficial action in paraffin base turbine oils was observed by Hatta [74, 1925] from laboratory tests at 120° C.; lead tetraethyl in amounts up to 0·2% decreased sludging and general deterioration. It appears, however, that the maximum effect with lead tetraethyl in oils is obtained at the high temperatures likely to occur, for example, in the combustion space of an air-cooled engine.

The presence of small amounts of tin and its compounds exerts an anti-oxidant effect in oils, delaying rise of acidity and formation of sludge. Experiments, the results of which are shown graphically in Fig. 7, were carried out by the author in a rotating cylindrical glass bulb heated isothermally in an electric furnace; 2 g. of oil were oxidized on the walls of the bulb, and measurements of oxygen absorption, sludging, acidity, and viscosity, &c., were made from time to time.

Tin varies in effect with temperature and with the variety of the oil, but for some reason, yet unexplained, tends in most circumstances to retard oxidation and postpone sludging, rise of acidity, and formation of carbon deposits.

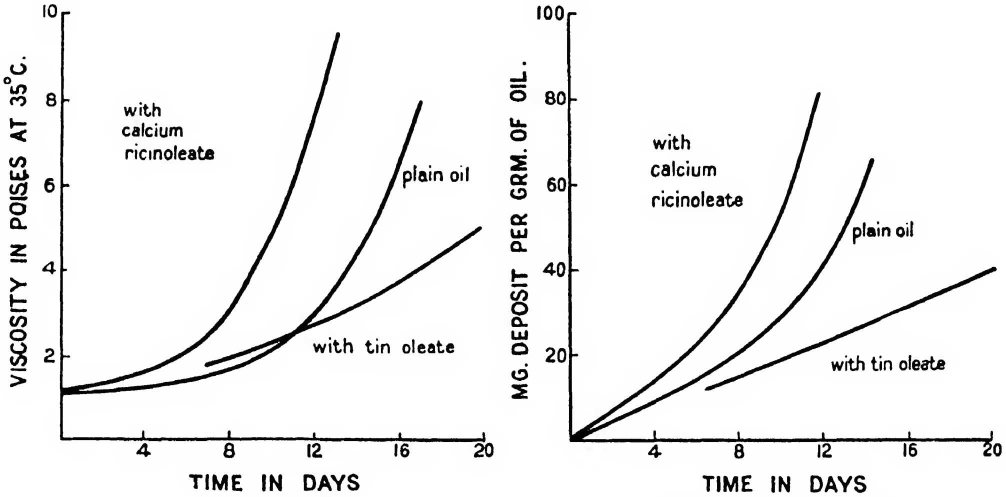
Yamada [150, 1930] has found 0·1% tin naphthenate to be beneficial in transformer oil as an anti-sludge; he carried out experiments with various oils heated in beakers at 140° for 100 hours with polished metal strips suspended in the oil.

The anti-sludge action of tin was shared with zinc and magnesium.

Some metals, although they do not retard oxidation but might possibly increase it slightly, were yet found by the rotating bulb method to have some beneficial action in oil, possibly by delaying acidity or altering the course of oxidation in favour of less sludging; such are chromium, mercury, cerium, and possibly magnesium.

Small quantities of polymerized styrene or indene have been suggested as stabilizing agents in lubricating oil (B.P. 379,717); also hydrogenated glyoxalines free from strongly negative groups (U.S.P. 1,805,953).

The anti-oxidants for oils, apart from the metallic compounds, belong mainly to the phenolic class or are organic bases such as the amines, urea, oxamide, aldehyde-ammonias, piperazine, hexamine, or ammonia itself. Lederer and Zublin [87, 1930] have discussed the problem of doped lubricating oils from the standpoint of laboratory tests. They direct attention to the fact that in engine trials the behaviour of an oil containing say 1% urea is no better than that of the plain oil, although the laboratory tests show a considerable improvement in the stability of the treated oil towards oxygen. Similarly some turbine oils, which by the laboratory tests show greater susceptibility to oxidation, form less sludge than more stable oils. These anomalies indicate that the final judgement regarding the worth of an oil anti-oxidant must be reached by practical tests in the same way that fuel anti-oxidants must be appraised by actual storage tests and anti-knocks by engine tests. The sensitivity of anti-oxidants to change of conditions render the laboratory experiments of limited value, although, of course, they serve to indicate likely substances and their scope.



(*a*) Viscosity. (*b*) Formation of deposits.

FIG. 7. Effect of calcium ricinoleate (0·5%) and tin oleate (0·5%) on the oxidation of a sample of Venezuelan asphaltic base red oil at 160° C.

Use of Oxidants in the preparation of Chemical Products from Petroleum as Raw Material.

The simple inclusion of oxygen into the paraffin hydrocarbon molecule results theoretically, according to the Armstrong-Bone hydroxylation theory of hydrocarbon oxidation, in the formation of a primary alcohol, which by further oxidation passes into the corresponding aldehyde.

$$\underset{\text{methane}}{2CH_4+O_2} = \underset{\text{methyl alcohol}}{2CH_3OH} \qquad \text{(I)}$$

$$\underset{\text{methyl alcohol}}{2CH_3OH+O_2} = \underset{\text{formaldehyde}}{2H\cdot CHO}+H_2O. \qquad \text{(II)}$$

Both alcohols and aldehydes find use in the cellulose, synthetic resin, and other industries, so the 'fixation' of atmospheric oxygen by petroleum hydrocarbons, such as methane of natural gas, is an important proposition.

Despite the simplicity of the chemical equations, there is yet no economically successful manufacture of alcohols and aldehydes in this way [23, 1924; 24, 1928; 98, 1932; 136, 1932]. The chief difficulty is the inertness of paraffin hydrocarbons to oxidation; the drastic conditions of oxidation cause poor yields, the alcohols and aldehydes which are formed tending to decompose thermally or to oxidize further to water and carbon dioxide.

Oxidants, such as ozone, nitrogen peroxide, or catalytic surfaces are employed in order to avoid high temperatures and to increase the oxidation rate. The same oxidants are also employed to facilitate the oxidation of liquid and solid hydrocarbons such as the residual oils or paraffin wax: fatty acids can be prepared from them and in the form of metal soaps are employed as detergents and paint driers, or in the form of esters as useful solvents and plasticizers in the cellulose industry. It is recorded that during the War, 1914–18, approximately 6,000 tons of the ethyl esters of fatty acids derived from the oxidation of hydrocarbons were prepared by Harries's method of ozonization, and these esters were used as food owing to shortage of fats in Germany [30, 1934]. The pungent condensate obtained from the oxidation of paraffin hydrocarbons is now employed in U.S.A. as a spirit denaturant. The sulphonated organic acids derived from oil residues by oxidation are recommended for use as activating ingredients in insecticides or as ore flotation or frothing oils. Processes of oxidation of petroleum under carefully controlled conditions are also carried out or are being developed for the purpose of stimulating 'cracking' of petroleum residues [8, 1932], of increasing the knock rating of a paraffinic fuel by partial oxidation, of obtaining maximum yields of lamp black, and of obtaining the useful gases, carbon monoxide, hydrogen, acetylene, carbon dioxide (dry ice), &c. from natural gas.

The oxidants used in such processes will be considered under separate headings: (*a*) ozone, (*b*) nitrogen peroxide, and (*c*) surfaces.

(*a*) **Use of Ozone.** A study of the use of ozone as an oxidant in the preparation of formaldehyde from methane has been made by Wheeler and Blair [147, 1922], Drugman [46, 1906], and earlier workers, but it appears that there is little prospect of a successful industrial process because of the low yield of formaldehyde obtainable compared with the large amount of ozone consumed.

The formation of formaldehyde is claimed when air and methane are passed through tubes containing silver or copper oxide catalysts under the influence of a high tension (80,000–90,000 volts) and a high frequency (400,000 cycles) electric field. Conversion yields of from 26% to 36% are claimed by this method (Marek and Hahn [98], p. 184).

Harries [72, 1909] treated liquid ethylene diluted with methyl chloride with 7% ozone-oxygen mixture and was able to isolate the normal ozonide which was decomposed by water into formaldehyde. A method of preparing formaldehyde, using ethylene, ozonized air, and water vapour, is claimed in U.S. Patent 1,423,753. Blair and Wheeler [14, 1923] passed mixtures of ethylene and oxygen containing 3% ethylene through an ozonizer. When the concentration of ozone was less than 1 c.c. per litre of mixed gases, 90% yields of formaldehyde based on the ozone were obtained. Lower yields were obtained with higher concentrations of ozone. Researches on the oxidation of higher olefines with the use of ozone have been carried out by Briner and colleagues [21, 1929].

According to Ger. Patent 344,615, excellent yields of formaldehyde and glycol are obtainable by passing ozonized air, mixed with ethylene and a spray of finely divided water particles, over contact bodies at temperatures between 20° and 100° C.

Using high pressures both methyl alcohol and formaldehyde are obtainable from methane with excess oxygen or ozonized air in the presence of porous non-metallic surfaces such as pumice, brick, slag, asbestos, &c. [6, 1922].

(*b*) **Use of Nitrogen Peroxides, Chlorine, &c.** It appears that monatomic oxygen available either from ozone or nitrogen peroxide favours the production of methyl alcohol from methane and, because of this, numerous investigations have been carried out with the use of nitrogen oxides as oxidants. Nitrogenous impurities are, however, an obstacle to the development of processes employing nitrogen peroxide as an oxidant. From experiments by Smith and Milner [127, 1931] and Layng and Soukup [85, 1928], the volume of formaldehyde gas formed was never more than the volumes of oxides of nitrogen used. Bibb and Lucas [13, 1929] describe experiments on the partial oxidation of natural gas by air with oxides of nitrogen; for satisfactory yields of formaldehyde they found that the gases must pass rapidly through the heating zone (less than 0·5 sec.) at the temperature range 700–750° C. Under similar conditions, benzene was found to be oxidized to phenol, 5% to 5·5% of the benzene being converted. The oxidant action of nitrogen peroxide is considered by Bibb to be explicable on a radiation hypothesis; the nitrogen peroxide becomes activated by absorption of radiation and then reacts to give monatomic oxygen. Frolich, Harrington, and Waitt [66, 1928] oxidizing methane directly by nitrogen peroxide failed to obtain any methanol. Smith and Milner suggest that methane first forms a loose compound with the nitrogen peroxide which then breaks down thermally into formaldehyde.

In the presence of nitrogen oxides the reaction between acetylene and oxygen proceeds as a homogeneous reaction producing trimeric glyoxal as the major product of reaction [89, 1931].

Bibb [12, 1932] carried out experiments with propane and other hydrocarbons and, by using nitrogen oxides with air, succeeded in one treatment of 1,000 litres of vapour in obtaining a yield of 19·8 lb. of 40% formaldehyde per 1,000 cu. ft. and, under some conditions, as much as 16% of the original weight of vapour.

In U.S. Patent 1,788,799, 13 Jan. 1931, is claimed the production of oxidation products from crude paraffin hydrocarbons, waxes, and the like, by acting with gases containing oxygen and nitrogen oxides in the presence of filler bodies with a large superficial area and of a metal enolate. It is agreed by most workers that the oxidants, ozone and nitrogen oxides, are far more effective than surface catalysts. A process of oxidation using chlorine as an oxidant is claimed in U.S. Patents 1,697,105 and 1,697,106 by Carmen [34, 1929] and Carmen and Chilton [35, 1929]. Carbon dioxide, sulphur dioxide, and sulphur trioxide have no oxidant action according to the experiments of Berl and Fischer [9, 1923].

(*c*) **Catalytic Surfaces.** The oxidation of petroleum hydrocarbons by air or oxygen, both in the liquid and gaseous phases in the presence of catalytic surfaces, is described in detail with bibliography by Burwell [30, 1934], Marek and Hahn [98, 1932], F. Hebler [77, 1928], Salway and Williams [122, 1922] (see also reports on the progress of naphthology, *J.I.P.T.*, 1933 and 1934).

Many of the processes are as yet undeveloped or are on a small scale and information is very meagre regarding the chemical character of the changes and the general success of the industrial undertakings. Burrell [29, 1930] has mentioned the interesting fact that the Empire Refining Co. produced daily by their process of oxidizing natural gas 70,000 gal. of a mixture comprising methanol, formaldehyde, and acetaldehyde. This mixture of oxygenated compounds was formed as a by-product during a process of removing the small proportion of air from natural gas prior to transmission through long pipelines in order to minimize inside corrosion of the steel.

Marek and Hahn consider that the wide variety of catalytic surfaces that have been proposed for the various oxidation processes throws some doubt on the real necessity for having a specific catalyst present in order to obtain the desired reaction rates. Indeed the claim for such a catalyst as borax-coated copper (B.P. 321,494 (1928)), makes it seem that the chief function of the catalytic surface is to distribute or help dissipate the heat generated by the reaction and prevent localized high temperatures which would jeopardize the continued existence of the desired intermediate oxidation product. Some investigators consider that certain catalytic surfaces favour the formation of particular oxygenated compounds, whilst, on the other hand, other workers consider that surfaces decrease the yield by favouring the formation of water and carbon dioxide.

REFERENCES

1. Aldrich, E. W., and Robie, N. P. *J.S.A.E.* **27**(t), 198 (1932).
2. Arrhenius. *Z. phys. Chem.* **4**, 226 (1889).
3. Austin Taylor, H., and Riblett, E. W. *J Phys. Chem.* 2667 (1931).
4. Bach. *Compt. rend.* **124**, 95 (1897).
5. Bäckstrom, H. L. J. *Meddel. f. k. Vet.-Akad. Nobel institut.* **6**, no. 15 (1927); *J.A.C.S.* **49**, 1460 (1927); *Trans. Faraday Soc.* **24**, 601 (1928).
6. Bakelite Ges. G.P. 421,215 (9 Nov. 1925).
7. Banks, F. R. *Royal Aer. Soc.*, London, Reprint 72 (1934).
8. Beall, N. *Refiner*, **11**, 390, 422 (1932).
9. Berl, E., and Fischer, H. *Z. Angew. Chem.* **36**, 297 (1923).
10. Berl, E., Heise, K., and Winnacker, K. *Z. phys. Chem.* Haber Band, Abt. A. 139, Bd. 453 (1928).
11. Bespolov, I. E., and Degtyareva, A. *Chem. Abs.* **26**, 5744 (1932).
12. Bibb, C. H. *Ind. Eng. Chem.* **24**, 10 (1932).
13. Bibb, C. H., and Lucas, H. J. *Ind. Eng. Chem.* **21**, 633 (1929).
14. Blair, E. W., and Wheeler, T. S. *J.S.C.I.* **42**, 343 t (1923).
15. Bone, W. A. *J.S.C.I.* **52**, no. 28, 202 (1933).
16. —— *Proc. Roy. Soc., A.*, Bakerian lecture, **137**, 243 (1932).
17. Bone, W. A., Fraser, R. P., and Witt, F. *Proc. Roy. Soc., A.*, **114**, 642 (1924).
18. Bone, W. A., and Hill, S. G. *Proc. Roy. Soc., A.*, **129**, 434 (1930).
19. Boyd, T. A. *Ind. Eng. Chem.* **16**, 893 (1924).
20. Bridgeman, O. *Oil and Gas J.* **31**, no. 3, 55 (1932).
21. Briner, E., and others. *Helv. Chim. Acta*, **12**, 154, 181, 529 (1929).
22. Brooks, B. T. *Ind. Eng. Chem.* **18**, 1198 (1926).
23. —— *Ind. Eng. Chem.* **16**, 185 (1924).
24. —— *J.I.P.T.* **14**, 738 (1928).
25. Brooks, D. B. *J.I.P.T.* **19**, 835 (1933).
26. Brunner, M. *Helv. Chim. Acta*, **13**, 197 (1930).
27. Brunner, M., and Rideal, E. K. *J.C.S.* 1162 (1928).
28. Burke. Canad. P. 339,715 (1934).
29. Burrell. *Nat. Petr. News*, **22**, no. 22, 80 (1930).
30. Burwell, A. W. *Ind. Eng. Chem.* **26**, 204 (1934).
31. Calcott, W. S., and Lea, J. E. U.S.P. 1,789,302 (20 Jan. 1931).
32. Callendar, H. L., and others. *Engineering* (4, 11, and 18 Feb. 1927); *Aer. Res. Comm. R. and M.* 1013 and 1062 (1926 and 1927).
33. Callendar, H. L., King, R. O., and Mardles, E. W. J. B.P. 295,230 (7 Aug. 1928).
34. Carmen, F. U.S.P. 1,697,105 (1 Jan. 1929).
35. Carmen, F., and Chilton. U.S.P. 1,697,106 (1 Jan. 1929).
36. Carr, M. S., and Brown, G. G. *Ind. Eng. Chem.* **21**, 1071 (1929).
37. Carter, C., and Coxe, A. U.S.P. 1,423,753 (25 July, 1922).
38. Charch, W. H., Mack, E., and Boord, C. E. *Ind. Eng. Chem.* **18**, 334 (1926).
39. Chavanne, G. *Chimie et Industrie*, **25**, 120 (1931).
40. Chavanne, G., and Bode, E. *J.A.C.S.* **52**, 1609 (1930).
41. Chebotar, L. P. *J.I.P.T.* no. 124, **20**, 168 (1934).
42. Christiansen, J. *J. Phys. Chem.* **28**, 145 (1924).
43. Coffey, S., and Birchall, T. *J.S.C.I.* **53**, 245 (1934).
44. Dhar, N. *Trans. Faraday Soc.* **24**, 567 (1928).
45. Dixon, H. B. *Rec. trav. chim.* **44**, 305 (1925).
46. Drugman. *J.C.S.* **89**, 660, 939 (1906).
47. Dumanois, P. *Compt. rend.* **186**, 292 (1928).
48. Dumanois, P., Mondain-Monval, P., and Quanquin, B. *Compt. rend.* **192**, 1158 (1931).

48*a*. —— —— —— *Ann. des comb. liquides*, 915 (1930).

49. Dupont, G., and Allard, J. *Bull. Soc. chim. de France*, 1216 (1930).
50. Egerton, A. C. Supplement to *Nature*, 7 July, p. 20 (1928).
51. Egerton, A. C., and Barton, C. H. B.P. 300,156 (6 Aug. 1927).
52. Egerton, A., and Gates, S. F. *Aero. Res. Com. Reports and Mem.* 1079 (1927).
53. —— —— *J.I.P.T.* **13**, 256 (1927).
54. Egerton, A. C., and Pidgeon, L. M. *Nature.* **127**, 391 (1931).
55. Egerton, A. C., and Ubbelohde, A. R. *Nature*, **133**, 179 (1934).
56. Egloff, G., and others. *Ind. Eng. Chem.* **25**, 804 (1933).
57. Egloff, G., Faragher, W. F., and Morrell, J. C. *Oil and Gas J.* **28** (29), 116 (8 Dec. 1929).
58. Egloff, G., Morrell, J. C., Lowry, C. D., and Dryer, C. G. *Proc. World Petr. Cong.* **2**, 50, 1933; with Wirth, C., and Murphy, G., ibid., **2**, 85, 1933.
59. Egloff, G., Morrell, J. C., Lowry, C. D., and Dryer, C. G. *Proc. World Petr. Cong.* **2**, 50, 1933; with Wirth, C., and Murphy, G., ibid., 1933, **2**, 85; *Ind. Eng. Chem.* **24**, 1375 (1932).
60. Elkington, H. D. B.P. 312,245 (17 Jan. 1928).
61. Engler. *Vorgänge der Autoxidation.* Brunswick (1904).
62. Flood, D. T., Hladky, J. W., and Edgar, G. *Ind. Eng. Chem.* **25**, 1234 (1934).
63. Fort, R., and Hinshelwood, C. N. *Proc. Roy. Soc.* **127a**, 218 (1930).
64. Francis, F. *J.C.S.* **121**, 496 (1922).
65. Frear, G. L. *J.A.C.S.* **56**, 305 (1934).
66. Frolich, P. K., Harrington, P. J., and Waitt, A. H. *J.A.C.S.* **50**, 3216 (1928).
67. Garner, F. H., Evans, E. G., Sprake, C. H., and Broom, W. E. J. *Proc. World Petr. Cong.* 1933, **2**, 170.
68. Gill, F., Mardles, E. W. J., and Tett, H. C. *Trans. Faraday Soc.* **24**, no. 90, Pt. II, 574 (1928).
69. Grebel, A. *Chimie et Industrie*, **22**, 473 (1929).
70. Greenbank, G. R., and Holm, G. E. *Ind. Eng. Chem.* **26**, 243 (1934).
71. Grün, A. *Ber.* **53**, 987 (1920).
72. Harries, C., and Koetschau, R. *Ber.* **42**, 3305 (1909).
73. Haslam, R. T., and Frolich, P. K. *Ind. Eng. Chem.* **19**, 292 (1927).
74. Hatta, S. *J.S.C.I.* (Japan), **28**, 1346 (1925).
75. Hebl, L. E., and Rendel, T. B. *J.I.P.T.* **18**, 187 (1932).
76. Hebl, L. E., Rendel, T. B., and Garton, F. L. *Ind. Eng. Chem.* **25**, 187 (1933).
77. Hebler, F. *Erdöl und Teer*, **19**, 333 (1928).
78. Hinshelwood, C. N. *Kinetics of chemical Change in gaseous Systems.* Clarendon Press, Oxford (1933).
79. Hoffert, W. H., and Claxton, G. *Proc. World Petr. Cong.* **2**, 69, 1933.
80. —— —— *Reports of the Benzole Research Committee of the Nat. Benz. Assn. and University of Leeds* (1926–30).
81. Jaeger, A. O. U.S.P. 1,908,705 (16 May 1933); U.S.P. 1,914,509 (20 June, 1933).
82. Johnson, J. Y. B.P. 379,717 (29 Aug. 1932).
83. King, R. O. *Engineering* (25 Aug. 1933).
84. Kogerman, R. N. *J.I.P.T.* **13**, 612 (1927).
85. Layng, T. E., and Soukup, R. *Ind. Eng. Chem.* **20**, 1052 (1928).
86. Layng, T. E., and Youker, M. A. *Ind. Eng. Chem.* **20**, 1048 (1928).
87. Lederer, E. T., and Zublin, E. W. *Nat. Petr. News*, **22**, 63 (13 Aug. 1930).
88. Le Mesurier, L. J. *J.I.P.T.* **17**, 414 (1931).
89. Lenher, S. *J.A.C.S.* **53**, 2420, 3737, 3752 (1931); **54**, 1830 (1932); **53**, 2962 (1931).

90. Lewis, S. *J.C.S.* **131**, 2241 (1930).
91. Lovell, W. G., Campbell, J. M., Signaigo, F. K., and Boyd, T. A. *Ind. Eng. Chem.* **26**, 475 (1934).
92. Manning, A. B. *Proc. World Petr. Cong.* **2**, 7, 1933.
93. Mardles, E. W. J. *J.C.S.* 872 (1928); *Compt. rend. réunion int. de chimie physique*, 503 (1928).
94. —— *Trans. Faraday Soc.* **27**, 681 (1931).
95. —— *Proc. World Petr. Cong.* **2**, 57, 1933.
96. Mardles, E. W. J., and Moss, H. *J.P.T.* **15**, 657 (1929).
97. —— —— *Proc. World Petr. Cong.* **2**, 116, 1933.
98. Marek, L. F., and Hahn, D. A. *The Catalytic Oxidation of Organic Compounds in the Vapour Phase.* Chem. Soc. Monograph Series Chemical Catalog Co. N.Y. (1932).
99. Martin, S. M., Gruse, W. A., and Lowy, A. *Ind. Eng. Chem.* **25**, 381 (1933).
100. Masson, H. J., and Hamilton, W. F. *Ind. Eng. Chem.* **21**, 544 (1929).
101. Midgley, T., and Boyd, T. A. *Ind. Eng. Chem.* **15**, 421 (1923).
102. Milas, N. A. *Chem. Rev.* **10**, 295 (1932).
103. Morrell, J. C., Dryer, C. G., Lowry, C. D., and Egloff, G. *Ind. Eng. Chem.* **26**, 497 (1934).
104. Moureu, C. *Report 2nd Solvay Council of Int. Chem.* 554 (April 1925).
105. —— *Trans. Faraday Soc.* **24**, 707 (1928).
106. Moureu, C., and Dufraisse, C. Messel Memorial Lecture, *Journ. Soc. Chem. Ind.* **47**, nos. 32 and 33 (1928).
107. Moureu, C., Dufraisse, C., and Chaux, R. *Compt. rend.* **184**, 413 (1927).
108. Nagai, Y. *J.C.S., Japan* **33**, 296 (1930).
109. Naylor, C. A., and Wheeler, R. V. *J.C.S.* 1240 (1933).
110. Norrish, R., and Smith, F. *Trans. Faraday Soc.* **24**, 620 (1928).
111. Ormandy, W. R., and Craven, E. C. *J.I.P.T.* **10**, 335 (1924).
112. Pease, R. N. *J.A.C.S.* **51**, 1839 (1929).
113. Perrin, F. *Compt. rend.* **184**, 1121 (1927).
114. Plauson's Forschungsinstitut. G.P. 344,615 (26 Nov. 1921).
115. Pope, J. C., Dykstra, F. J., and Edgar, G. *J.A.C.S.* **51**, 1875, 2203, 2213 (1929).
116. Prettre, M. *Compt. rend.* **196**, 1891 (1933).
117. Prettre, M., Dumanois, P., and Laffitte, P. *Compt. rend.* **191**, 329, 414 (1930).
118. Ramsey, J. *Ind. Eng. Chem.* **24**, 539 (1932).
119. Rogers, T. H., Bussies, J. L., and Ward, P. T. *Ind. Eng. Chem.* **25**, 397 (1933).
120. Rogers, T. H., and Voorhees, V. *Proc. World Petr. Cong.* **2**, 63, 1933.
121. Rosenstein, L., and Hund, W. U.S.P. 1,835,184 (2 Aug. 1931).
122. Salway, A., and Williams, P. *J.C.S.* **122**, 1343 (1922).
123. Schaad, R. E., and Boord, C. E. *Ind. Eng. Chem.* **21**, 756 (1929).
124. Scheumann. *Nat. Petr. News*, **25** (14), 29, 72 (15 April, 1933).
125. Schmidt, A. W. *Proc. World Petr. Cong.* 1933, **2**, 181.
126. Semenoff. *Z. Physik Chem.*, **48**, 571 (1928).
127. Smith, D. F., and Milner, R. T. *Ind. Eng. Chem.* **23**, 357 (1931).
128. Somerville. B.P. 289,347 (26 Oct. 1926).
129. Souders, M., and Brown, G. *Ind. Eng. Chem.* **21**, 1261 (1929).
130. Standard Oil Co. B.P. 348,011 (29 Oct. 1929).
131. Staudinger, H. *Ber.* **53** B, 1075 (1925).
132. Stephens, H. N. *J.A.C.S.* **50**, 568 (1928).
133. —— *J. Phys. Chem.* **37**, 209 (1933).
134. Storey, L. G., Provine, R. W., and Bennett, H. T. *Ind. Eng. Chem.* **21**, 1079 (1929).
135. Sullivan. *Oil and Gas J.* **29** (42), 156 (5 March 1931).
136. Symposium on utilization of gaseous hydrocarbons. *Ind. Eng. Chem.* **24**, 10 (1932).
137. Taylor. *J. Phys. Chem.* **27**, 322 (1923).
138. Thomas, W. H. *Proc. World Petr. Cong.* **2**, 44, 1933.
139. Thompson, H. W., and Hinshelwood, C. N. *Proc. Roy. Soc.* **125** A, 277 (1929).
140. Tizard, H., and Pye, D. R. *Phil. Mag.* **44**, 79 (1922).
141. Townend, D. T. A., and Mandlekar, M. R. *Proc. Roy. Soc.* **141** A, 484 (1933).
142. Tuichinin, B. C., and Ivanov, K. I. *J.I.P.T.*, Abstract 364, **158** A (1931).
143. Wagnfr, C. and Hyman, J. *J.I.P.T.* **15**, no. 77, 674 (1929).
144. Ward, A. *Oil and Gas J.* **31**, no. 12, 16 (1932).
145. Ward, A., Jordan, C., and Fulweiler, W. *Ind. Eng. Chem.* **25**, 1224 (1933).
146. Weerman, R. A. *J.I.P.T.* **13**, 300 (1927).
147. Wheeler, P. S., and Blair, E. W. *J.S.C.I.* **41**, 331 (1922).
148. Wiezevich, P. J., and Frolich, P. K. *Ind. Eng. Chem.* **26**, 267 (1934).
149. Winning, C., and Thomas, R. M. *Ind. Eng. Chem.* **25**, 511 (1933).
150. Yamada. *J.S.C.I. Japan*, **36**, 176, 277 (1933); **33**, 113 (1930); **34**, 188 (1931).
151. Yamaguchi, B. *Reports Aer. Inst. Tokyo*, **5**, nos. 61 and 65 (1930).
152. Yoshikawa, K. *Bull. Inst. Phys. Chem. Res. Japan.*, **10**, 305 (1931).
153. Yule, J. A. C., and Wilson, C. P. *Ind. Eng. Chem.* **23**, 1254 (1931).

14. RESEARCHES ON DETONATION IN FRANCE

By Dr. P. DUMANOIS

Aeronautical Inspector-General, Hon. Director of Aerial Construction, Hon. M.Inst.P.T.

THE manifest shock occasioned by knocking (detonation) led the author and his associates from the first, in agreement with Dixon and with Tizard, to distinguish 'knock' both from auto-ignition by adiabatic compression and from auto-ignition by a hot-spot, and to attribute the phenomenon to the explosive wave discovered by Berthelot and Vieille, and to give it the name undulatory combustion [2, 1926].

A verification of this hypothesis has been obtained by so altering an engine that a series of sudden increases in cross-section occur along the path of propagation of the flame. It is possible in this way to raise the compression of a four-cylinder automobile engine from 4·6 to 6·7 using a mixture of 77% gasoline and 23% kerosine [3, 1926]. This purely physical line of research is thought to be fertile and worth following up. But the really interesting point was to find out why, after a certain period of regular combustion, this state of undulatory combustion was set up. The first hypothesis consisted in supposing that as a result of the regular propagation of flame and the consequent rise of pressure and temperature, a layer of the mixture could at a certain moment be raised to sufficient temperature to burn instantaneously, and so set up the wave mechanism.

The facts that increase of initial pressure had only a slight influence on the length of run of the ordinary combustion [8, 1926], and that the presence of lead tetraethyl neither modifies the length of the regular combustion, as has been shown by Egerton and Gates, nor the velocity of the explosion wave [9, 1928], led the authors to look for the cause of detonation in a chemical property particular to the fuel. It was thought that this might be found on the basis of the researches of MM. Moureu, Dufraisse, and Chaux, who applied the result of their work on anti-oxidants to the problem of knock, and who attributed the phenomenon of detonation to the formation of peroxides, which they found under certain conditions in an engine [15, 1927].

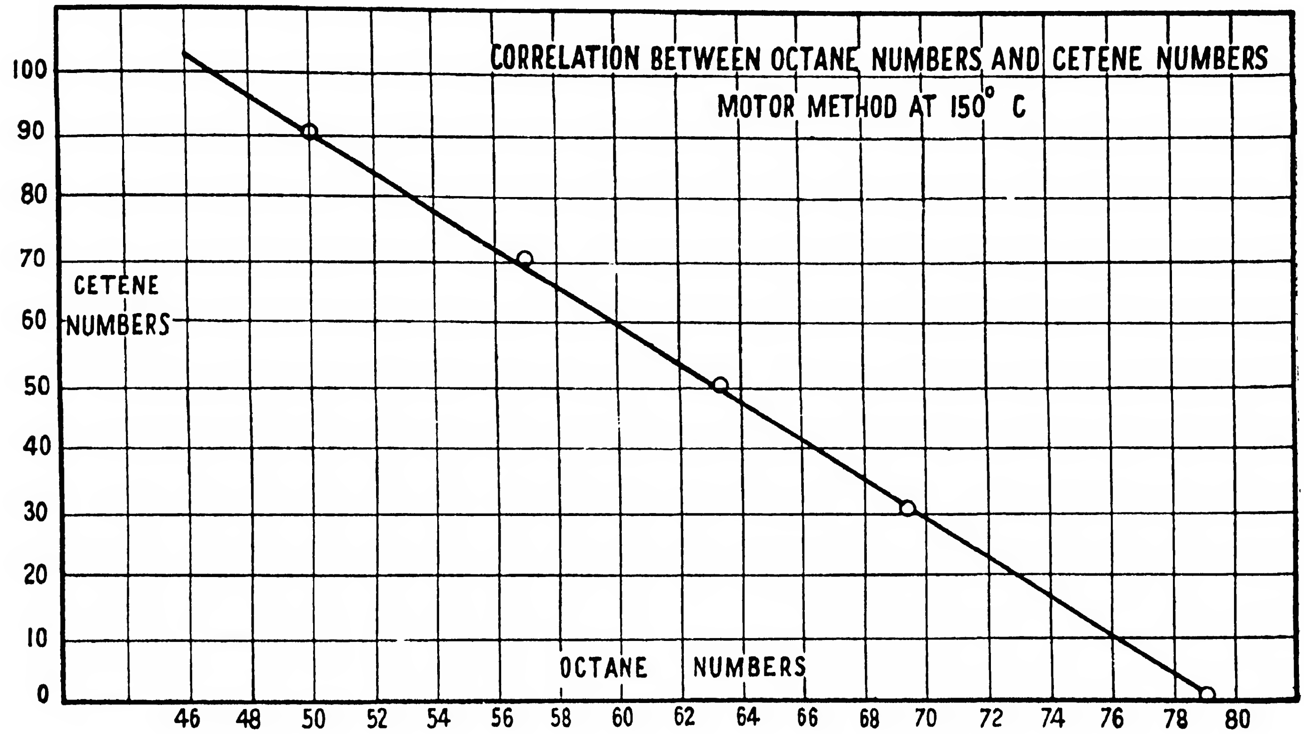
At the outset a confirmation was obtained from the retarding effect on ignition by anti-knocks [4, 1926], and from the fact that the lead tetraethyl diminished the tendency for pre-ignition [5, 1928]. Owing to the criticisms to which this peroxide theory gave rise, attempts were made to show quite irrefutably their existence in fuel mixtures. First the time scale of the oxidation was altered and by progressively heating a fuel mixture in a bomb a phenomenon analogous to that of adiabatic compression was produced [11, 1928]. These experiments, made in collaboration with M. Mondain-Monval, showed that a reaction set in at 100° C. with a diminution in the number of molecules, and the products so formed decomposed violently at a temperature about 220° C. The addition of traces of lead tetraethyl produced a definite lessening of the effect.

M. Mondain-Monval, continuing these researches with M. Quanquin, was able by direct oxidation of fuel at atmospheric pressure to produce at about 200° C. appreciable amounts of peroxides [12, 1929]. The possibility of formation of these having been thus shown, the attempt was made to demonstrate their presence during the running of an engine by suddenly cutting off the ignition of a single-cylinder engine as soon as it was detonating, and driving the engine electrically; aldehydes and peroxides were found in the exhaust [13, 1931]. Moreover, as it was found from these experiments that the peroxides were all decomposed at temperatures lower than 300° C., the question of what would happen if the fuel was first heated to higher temperature than 300° C. was investigated in collaboration with M. Laffitte. MM. Laffitte and Prettre showed that a fuel has two ignition temperatures, one about 300° C. and the other in the neighbourhood of 600° C. The first disappeared when the mixture contained lead tetraethyl [10, 1930]. It was thought, therefore, that if the fuel introduced into a spark-ignition engine were to be raised to a sufficient temperature the zone of formation and decomposition of peroxides might be passed through sufficiently rapidly and detonation ought to disappear. This result was confirmed, in collaboration with MM. Bonnier and Moynot [6, 1933], using a C.F.R. engine running at 650 r.p.m., the coolant being at 150° C. As the pressure increased detonation was obtained, and if further increased detonation rose in intensity as the temperature of the walls of the combustion chamber increased. The engine then turned over quietly and the power diminished. If the ignition was cut off, the functioning continued for some time, the temperature of the walls rose rapidly, and then back-firing stopped the engine. M. Serruys, who has also studied this phenomenon, gives it another explanation, namely, that the disappearance of detonation is due to the fact that the rise of temperature of the walls causes pre-ignition before top dead centre; the combustion cannot then provide high enough pressures and temperatures to give rise to detonation [16, 1933].

These various results led the author to consider that the variable ignition delay with heavy fuels in injection engines should be sought also in the phenomena of oxidation. It was shown that the detonating fuels in spark-ignition engines are just those which do not produce knock in injection engines. The diminution in octane number produced by mixing with a given petrol 25% of a certain gas oil was investigated using a C.F.R. engine; this proportion allowed the engine to run as a spark-ignition engine. A number of gas oils were thus classified and the classification was found to conform with that of Boerlage and Broeze who related the delay in ignition with the cetene number [14, 1931]. In fact, the cetene number varies with the heptane number [7, 1933].

This method has been given effect to by M. Bonnier and his collaborators at the National Station of Bellevue: by strictly applying the 'motor method' of carrying out the tests, and utilizing a standard petrol having octane number 79, an anti-knock value of the fuel is found so much the lower as the gas oil possesses a higher octane number. The curve shows the correspondence between the octane number and the cetene number for a mixture of cetene and methylnaphthalene instead of gas oil. It will be noted that there is an accurately linear relationship. A difference of one octane number corresponds to a difference of three cetene numbers. Such is the precision of the method that it allows of the determination of the cetene number with the C.F.R. standard engine.

Summing up, detonation is deemed to be the result of undulatory combustion which is translated by means of pressure waves liberated by chemical processes; these processes are attributed to the production of peroxides which act either by exothermal decomposition or by their products of decomposition causing a lowering of the temperature of ignition. Furthermore, there is a relation between the role of lead tetraethyl as an anti-knock and its action as an inhibitor of oxidation. The peroxide theory has shown itself particularly fertile: it led to the prediction of results which experiments have confirmed, but it should not be supposed that in every case it is the unique cause of detonation. There are too many variables that cannot be isolated in the running of engines to suppose that a phenomenon, however preponderating its importance, should be the only one to intervene.



That being so, a résumé can be given of the researches of M. Serruys which led him to think that the liberation of the wave was produced towards the end of the combustion by the ignition of a nucleus of fuel under the influence of a rise of temperature and of pressure [17, 1934]. This conception, however, does not appear very different from the one put forward by the author in 1926 in which it was supposed that the wave was liberated after a certain period of regular combustion by the adiabatic ignition of a layer of the gas. According to M. Serruys, knocking has a certain definite physical characteristic (when its intensity is slight) which may be stated as follows: at the end of the combustion a small part of the fuel burns in a very short time, usually less than 1/10,000th of a second [18, 1933], and produces a strictly localized high excess pressure (causing heating of the gas and therefore of the walls) [19, 1932]. The gases which detonate and of which the pressure is very high then expand into the other parts of the combustion chamber, forming pressure waves. The intensity of these pressure waves rapidly diminishes with the distance from the source of detonation and diminishes also with the number of successive reflections. The velocity of propagation of these waves in the burnt gas appears to be about 500 metres per second for an engine of present-day design compression ratio 5·5 to 1 with petrol of 60 octane. These views agree with the hypothesis presented regarding the propagation of explosion waves [2, 1926] and with the work of M. Jouguet.

Present Orientation of Research.

Incontestably, the general use of the standard C.F.R. engine has been a considerable advance: a method of testing exists where previously there had been none. The method can certainly be improved. Moreover, using the C.F.R. engine, disagreements have eventuated, particularly concerning the classification of aviation fuels. This, however, is not surprising. The value of the 'motor method' from the point of view of the automobile arises from the fact that in America the conditions for use of the C.F.R. engine were determined so as to obtain the same classification for different fuels with those obtained in practice, employing many different engines and fuels. It is not surprising, therefore, that for aero-engines working under very different conditions the method does not give exact results. The situation is still more complicated when, instead of using hydrocarbons derived from petroleum, alcohol and benzene are added as in most European countries. These difficulties started from the very commencement of the employment of the C.F.R. motor and led M. Champseur to investigate a different method of finding the suitability of fuels for aero-engines.

As detonation results initially from an over-pressure, and as this over-pressure could give rise to increase of temperature, it can be realized that at the moment when detonation appears the thermal balance in the engine will change, the temperature of the walls will rise, and a quantity of heat will pass into the cooling water and a less quantity into the exhaust gas. The method devised by M. Champseur, which is described in *Publications Scientifiques et techniques du Ministère de l'air*, no. 17, is as follows:

> The mixtures are admitted at the normal throttle-opening, with the engine running at constant speed about 8/10ths of the normal (so as to obtain an appreciable detonation without imposing excessive strain on the engine) and with a mean temperature of the cooling water 65 to 70° C. Estimates of detonation are made by finding the difference of temperature between the inlet and outlet water, keeping the flow constant. The anti-knock qualities of the fuels are compared with the heavily detonating basic fuel to which an anti-knock ethyl fluid or benzole has been added. Rapid determinations are made, having suitably regulated the carburettor, (1) of the heating of the water by the fuel to be tested, and (2) of the heating curve of the water as a function of the proportions of anti-knock added to the basic fuel.

In practice it is sufficient to determine only a portion of the curve by observations at two points near together in such a way that the extreme ordinates are on either side of the ordinate corresponding to the heating provided by the fuel to be tested. It is possible so to find the percentage of the anti-knock which has to be added to the basic fuel to be equivalent to the fuel to be tested, and this characterizes its anti-knock quality. Actually the method is only valid for fuels of similar calorific power. For fuels of very different calorific power it would be necessary to correct the rise of the temperature of the water for the total energy of the explosive mixture.

Research at the National Station of Bellevue under M. Bonnier is now orientated towards the study of such thermal effects which are at least as harmful to an engine as mechanical effects. Research is directed towards finding whether the method using the bouncing pin gives results comparable to the thermal method. It is possible to simplify the latter in the case of the C.F.R. engine as all conditions are carefully fixed, and it is only necessary to follow the variations of the temperature of a thermocouple placed, for instance, at the joint of the bouncing pin.

There is another difficulty from the practical point of view which results from the choice of a reference fuel which limits the possibility of using compression pressures to those which are possible with a 100% octane fuel. At higher octane number than 90 the motor method gives uncertain results. An attempt has been made to overcome this difficulty by making mixtures with detonating fuels and then extrapolating, but the method is sensitive and at the present moment does not give any standard. The thermal method is preferred.

Finally, there is another line of work which is going on at the National Test Station of Bellevue which has considerable practical interest in connexion with the employment of a given engine with fuels of very high anti-knock value [1, 1934]. Up to the present, from the experiments made at Bellevue, it has been found that,

(1) in the zone where detonation is perceptible to the ear the temperature of the exhaust increases with the anti-knock value of the fuel, other conditions being the same,
(2) the variation is more rapid as the compression ratio rises,
(3) outside this zone, that is to say, when the detonation has practically ceased, the temperature of the exhaust remains practically constant whatever the anti-knock value of the fuel (at a constant richness of mixture), and
(4) the temperature of the exhaust decreases, of course, as the compression ratio is raised and the more rapidly the less the anti-knock value of the fuel.

The adoption of a fuel with very high anti-knock value does not have the same effect in all engines. For an engine which is normally detonating (as for many aero-engines, although the detonation may not be audible) the change of fuel produces a rise in the temperature of the exhaust. With engines less loaded, and little or not at all subjected to detonation, the variations of the temperature of exhaust are insignificant.

REFERENCES

1. *Ann. Comb. Liq.* 481, no. 3 (1934).
2. DUMANOIS, P. *Technique moderne*, **18**, no. 9, 257 (1 May 1926); **18**, no. 22, 673 (15 Nov. 1926).
3. —— *Compt. rend.* **182**, 1378 (1926).
4. —— *Compt. rend.* **182**, 1526 (1926).
5. —— *Compt. rend.* **186**, 292 (1928).
6. —— *Compt. rend.* **197**, 393 (1933).
7. —— *Compt. rend.* **196**, 1003 (1933).
8. DUMANOIS, P., et LAFFITTE, P. *Compt. rend.* **183**, 284 (1926).
9. —— —— *Compt. rend.* **186**, 146 (1928).
10. DUMANOIS, P., LAFFITTE, P., et PRETTRE, M. *Compt. rend.* **191**, 329, 414 (1930).
11. DUMANOIS, P., et MONDAIN-MONVAL, P. *Compt. rend.* **187**, 892 (1928).
12. —— —— *Compt. rend.* **189**, 761 (1929).
13. DUMANOIS, P., MONDAIN-MONVAL, P., et QUANQUIN, B. *Compt. rend.* **192**, 1158 (1931).
14. *Engineering*, 603, 3435 (1931); 687, 3438 (1931); 755, 3440 (1931).
15. MOUREU, C., DUFRAISSE, C., et CHAUX, R. *Compt. rend.* **184**, 413 (1927).
16. SERRUYS, M. *Compt. rend.* **197**, 224 (1933).
17. —— *Compt. rend.* **198**, 1574 (1934).
18. —— *Compt. rend.* **196**, 1083 (1933); **197**, 1296 (1933).
19. —— *Compt. rend.* **195**, 1376 (1932).

METHODS OF KNOCK RATING

15. MEASUREMENT OF THE KNOCKING CHARACTERISTICS OF AUTOMOTIVE FUELS

By JOHN M. CAMPBELL, B.S., and T. A. BOYD, B.Ch.E.
Research Laboratories Section, General Motors Corporation, Detroit, Michigan

WHEN gasoline is burned by explosion in a conventional spark-ignition engine, common experience has shown that if certain limits of compression pressure are exceeded there appears an abrupt change in the nature of the explosion. That is to say, the explosion which up to a certain point was comparatively noiseless is now accompanied by a distinct metallic noise, sounding as sharp as the blow of a hammer within the combustion chamber. This noise is commonly called knock.

Although there is still some uncertainty about the physical and chemical processes that cause the production of the mechanical noise which is generally defined as knock, it is a well-established fact that knock is accompanied by, or is caused by, a correspondingly rapid rise in pressure. This rapid inflammation of the last part of the charge to burn is indicated by a sudden transition from the relatively slow but orderly flame movement across the combustion chamber to what might be pictured as an almost instantaneous inflammation of the remainder of the charge. For a more complete discussion of this subject see the article on Theory of Knock in Internal-combustion Engines, by Beatty and Edgar.

The intensity of the knock as heard by an observer varies with the characteristics of the fuel supplied to the engine. Under a given set of operating conditions some fuels knock severely, others only lightly, and others not at all. This difference in tendency to emit sounds distinguishable to the ear as knock is used for grading commercial gasolines. The knocking tendency is thus a very real property of motor fuels and one upon which the consumer has a constant check by actual observation in service. For these reasons a uniform and accepted measure of this property is a practical necessity in the manufacture, the marketing, and the use of automotive fuels. The purpose of this discussion is to describe the development of the present accepted methods of rating fuels for knocking tendency and to discuss some problems attendant upon the subject of knock rating.

PART I. AUTOMOBILE FUELS

Historical Sketch.

Prior to the development of the present standard knock-testing procedure several different methods of rating automobile fuels were in use. The earliest of these were based upon the observation of knock in engines by ear. One of these was that of Ricardo [38, 1921] in which the knocking tendency of a fuel was expressed in terms of 'Highest Useful Compression Ratio', the latter being the highest compression ratio at which the engine could be operated on the fuel in question without audible knock. Another one of the early methods involved the form of instrumentation known as the bouncing-pin indicator for comparing knock intensities between different fuels [34, 1922]. Later a number of methods came into use in different laboratories. The principal types of these are listed in Table I. With such a wide diversity of methods among different laboratories, and with the growing importance of an accurate knowledge of knocking tendency in the marketing of motor fuels, it soon became apparent that there was an urgent need of a uniform and accepted knock-testing procedure capable of giving reproducible results among different laboratories.

In response to this demand, a group was formed in America early in 1928 for the purpose of developing a uniform knock-testing apparatus and procedure. This group was a sub-committee of the Co-operative Fuel Research Committee. The Co-operative Fuel Research Committee is composed of representatives of the American Petroleum Institute, the Automobile Manufacturers' Association (formerly the National Automobile Chamber of Commerce) as represented by the Society of Automotive Engineers, and the National Bureau of Standards. In carrying out its work this group has aimed to produce a method of test which would be universally applicable. To this end it was fortunate in having the co-operation of similar interested groups in England, France, Germany, and Holland. Since the formation of this committee, most of the research on knock testing which has been carried out in America has been made by members of the committee or under their auspices. Accordingly, the discussion which follows is essentially a record of the progress which has been made by this co-operative organization. Although space permits only a brief outline of this work to be given here, a complete account may be found in the literature in references [5, 1930; 6, 1931; 7, 1932; 8, 1933; 45, 1932; 46, 1934; 47, 1933; and 48, 1935].

Engine, Accessories, and Instrumentation.

At the time this standardization work was started, it was recognized that the first essential to a uniform knock-testing procedure was the provision of a standard engine. Attempts to rate fuels for knock in simpler and possibly more convenient laboratory apparatus, such as in bombs, in ignition temperature apparatus, or by chemical analysis, had not been successful. The engine which was evolved is a single-cylinder, valve-in-head, variable-compression engine having a 3¼-in. bore and a 4½-in. stroke. The engine is water cooled and is equipped with a three-bowl, variable-float-level carburettor and with means for automatically regulating the spark timing with changes in compression ratio. The power output of the engine is absorbed by a form of induction motor-generator which runs at constant speed—it operates as a motor to start the engine and as a generator to absorb the load and to control the speed when testing fuels. No attempt is made to measure the power.

The instrumentation used in comparing knock intensities is known as the bouncing-pin indicator (see Table I). In

TABLE I

Representative Methods that have been used for the Measurement of Knocking Characteristics

General method and reference	*Procedure*	*Knock controlled by*	*Method of measuring knock*	*Results expressed in terms of*
Variable compression [38, 40]	Determine compression ratio for incipient knock	Compression ratio	Audibility	H.U.C.R. (Highest Useful Compression Ratio)
Bouncing-pin [4, 25, 34]	Comparison of knock intensity with reference fuels	,,	Bouncing-pin	Reference fuels
Spark advance [39]	Determine spark advance for various knock intensities	Spark advance	Audibility	Index based on knock intensity
Spark advance [10]	Determine spark advance for maximum torque	Spark	Power	Spark advance
Diaphragm rupture [27]	Find time required to rupture diaphragm of known thickness when exposed to combustion chamber	Compression pressure	Time required to rupture diaphragm	Reference fuels
Variable throttle [13]	Determine I.H.P. at various rates of fuel flow at throttle setting for incipient knock	Throttle	Audibility	,, ,,
Variable throttle [49]	Determine power at throttle opening for incipient knock constant mixture ratio, speed, and spark	,,	,,	,, ,,
Variable throttle [30]	Find manifold vacuum at throttle setting for incipient knock at constant mixture ratio, speed, and spark	,,	,,	,, ,,
Audiometer [23]	Comparison of knock intensities between test fuels and reference fuels	Compression ratio	Audiometer	,, ,,
Audiometer [41]	Stroboscopic audiometer for comparison of knock intensities	,,	Strobophonometer	,, ,,
Temperature plug [21]	Comparison of temperature in plug located in cylinder	,,	Temperature of plug	,, ,,
Bomb [28]	Rate of pressure rise by optical indicator	Initial pressure	Pressure-time curve	..
Bomb [13]	Comparison of rates of pressure rise in bomb by means of bouncing-ball on diaphragm	,,	Height of bounce	..
Chemical analysis [18]	Estimation paraffin, naphthene, aromatic, and olefine content	..	..	Chemical analysis
Ignition temperature [3, 17, 32, 33, 44]	Various	..	..	..

this instrument a steel pin rests on a thin steel diaphragm which is in direct contact with the combustion chamber. When knock occurs the pin is given sufficient impulse to be driven upwards, thereby closing a pair of contacts and thus causing current to flow in an electric circuit containing a hot-wire element. The contacts are adjusted so that they do not close during non-knocking combustion. A thermocouple placed near the hot-wire element is connected to a millivoltmeter, the reading of which varies with the temperature of the wire, which temperature, in turn, varies with the knock intensity. This millivoltmeter is known as a knockmeter and is used, in conjunction with the bouncing-pin properly adjusted, for directly comparing the knock intensities caused by different fuels [6, 1931]. This instrumentation is in common use at the present time. It does not give an absolute measure of knock intensity; it merely gives a comparative indication of knock intensity between one fuel and another, or between the fuel under test and reference fuels of standard knock ratings that are always used as a means of making the measurements quantitative. Improvements in this form of instrumentation may be expected from time to time. Other methods which have been suggested and which are now under investigation at various laboratories involve microphonic pick-up of knock-sound intensity or measurement of rates of pressure rise by electric pressure indicators (see Table I).

Fig. 1 is a photograph of the assembled apparatus for knock testing in its present form. This apparatus is complete as illustrated and requires four service connexions, as follows: electric current for the power-absorbing unit, water for the cooling unit, a drain for cooling, water and an exhaust line.

Reference Fuels.

A second essential to a knock-testing method is a scale for measuring relative knocking tendency. This problem was solved by selecting the two hydrocarbons, normal heptane and *iso*-octane (2,2,4-trimethylpentane), as reference fuels, a suggestion made by Edgar [15] in 1927. Normal heptane is a hydrocarbon of very low anti-knock value and *iso*-octane is one of high anti-knock value; both are definite, reproducible compounds having similar physical characteristics. Using mixtures of these hydrocarbons as reference fuels having standard reproducible knocking tendency, the knocking tendency of any given fuel to be rated can be expressed in terms of an equivalent mixture of *iso*-octane and heptane. This is the octane number scale of knock rating. As defined in the present official procedure [1, 1934–5], the octane number of a motor fuel is the whole number nearest to the octane number of that mixture of *iso*-octane and normal heptane which the motor fuel matches in knock characteristics when compared in accordance with the accepted standard procedure. The octane number is defined by, and is numerically equal to, the percentage by volume of *iso*-octane (2,2,4-trimethylpentane) in a mixture of *iso*-octane and normal heptane, used as a primary standard for measurement of knock characteristics. Thus, by definition, normal heptane has an octane number of zero and *iso*-octane of 100.

On account of the relatively high cost of these primary

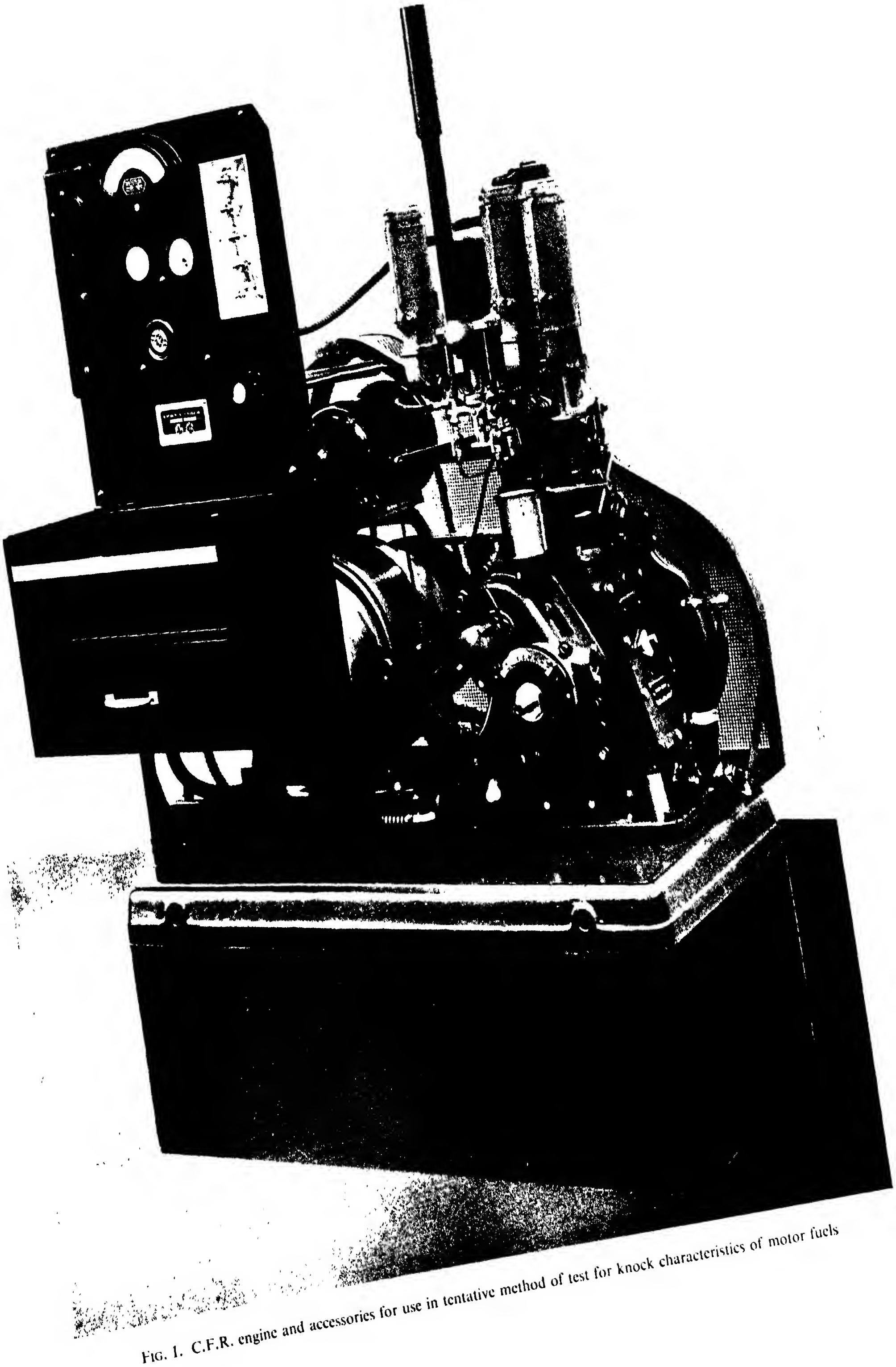


FIG. 1. C.F.R. engine and accessories for use in tentative method of test for knock characteristics of motor fuels

reference fuels, it has been customary in general laboratory testing to use secondary reference fuels. These have usually consisted of stable, straight-run gasolines, one of comparatively high knocking tendency and another of low knocking tendency. Mixtures of these have been carefully calibrated in terms of octane number directly against heptane and *iso*-octane. Experience has indicated that in making such calibrations it is desirable to use as many independent observations as possible and to average the results in order to obtain a maximum of precision in the final calibration [2, 1933]. Secondary reference fuels which have been calibrated in terms of octane number are available in America, and information with respect to them may be obtained from the Secretary of the Co-operative Fuel Research Committee, c/o The Society of Automotive Engineers, 29 West 39th Street, New York City.

Laboratory Procedure.

A definite and carefully controlled procedure is another essential element in a knock-testing method. Precise control of test conditions is necessary because knock is affected by a large number of engine variables. Some of the outstanding ones which have been reported by various investigators are:

1. Compression ratio [38, 1921].
2. Throttle opening [30, 1928].
3. Engine speed [42, 1929].
4. Spark timing [11, 1931; 42, 1929].
5. Mixture ratio [11, 1931; 42, 1929].
6. Mixture temperature [42, 1929].
7. Jacket temperature [16, 1927; 20, 1932; 36, 1935; 42, 1929].
8. Intake air temperature [9, 1931; 42, 1929].

In some of the earlier methods knock was expressed in terms of some one of these variables. Thus, as may be seen in Table I, Ricardo determined what was called the H.U.C.R. (Highest Useful Compression Ratio), which he defined as the compression ratio at which knock just becomes audible in a certain single-cylinder, variable-compression engine operated at 1,500 r.p.m. Other methods based upon such factors as the throttle setting and the spark timing at the point of incipient knock are indicated in Table I. An outstanding objection to these methods in general is that they have not resulted in the degree of reproducibility of results between different laboratories that is required. Some of them depend upon the evaluation of knock intensity by ear, a procedure which demands careful control of outside noises and prohibits the use of more than one engine in a room. Others based on power measurements are not sufficiently sensitive to slight differences in knock tendency.

After standardization of test equipment similar to that shown in Fig. 1 and the selection of heptane and *iso*-octane for reference fuels, a tentative standard procedure for knock testing was drawn up and widely used during the years 1931 and 1932 [6, 1931]. Briefly, this procedure involved the comparison of fuels with standard reference fuels in a single-cylinder engine using the bouncing-pin indicator as a means of comparing knock intensities. The engine conditions specified for this procedure were as follows:

1. Engine speed 600 r.p.m.
2. Full load (wide-open throttle).
3. Jacket temperature 212° F.
4. Spark advance for maximum power.
5. Mixture ratio for maximum knock.
6. Mixture temperature not specified, but no heat applied to mixture before entering the engine block.
7. Knock intensity approximately that obtained by raising the compression ratio one ratio above the compression ratio for first audible knock in a room where there are no other engines running.

The results of co-operative tests showed that from the viewpoint of reproducibility this method gave reasonably good results. Thus the average deviation from the mean for a number of co-operating laboratories in rating samples of gasoline directly against the primary standards, heptane and *iso*-octane, was less than one octane number, or the equivalent of 1% of *iso*-octane in heptane [6, 1931].

Correlation between Laboratory Ratings and Road Ratings.

Some of the engine variables which influence knock have been found to affect the knocking behaviour of different types of fuels to different degrees. This fact has given rise to a number of problems, the most outstanding of which is the matter of correlating road ratings with laboratory ratings. Road tests indicate that two widely different types of fuels which knock alike in one car may have appreciably different knock ratings in another make of car or even in another car of the same make. This is really what might be expected, when it is recognized that knock ratings made on the road in different cars may be obtained at widely different speeds, spark timings, mixture ratios, and mixture temperatures, and that the knocking tendencies of different fuels are not affected to the same degree by each of these variables. Figs. 2 and 3 show, for example, how mixture

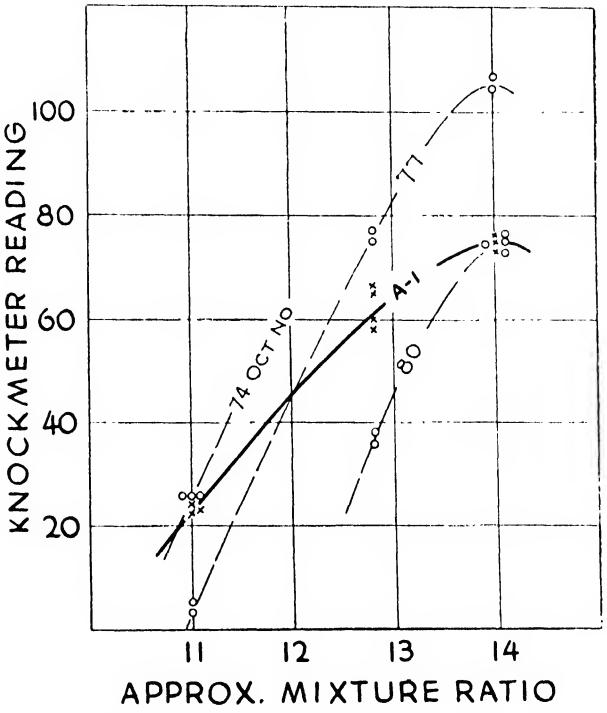


FIG. 2. Chart showing that, with fuels of different types, knocking tendency may be unequally affected by changes in mixture ratios. Single-cylinder, variable compression engine. Compression ratio 5·8. Spark 30° before top centre. Mixture 55–60° F. Jacket 212° F. Speed 750 r.p.m.

ratio and engine speed, respectively, may affect the relative knocking tendencies of two different types of fuel. From Fig. 2 it will be seen that at a mixture ratio of 14 lb. of air to 1 lb. of fuel, gasoline A 1 was equal in knocking tendency to a calibrated reference fuel of 80 octane number; but that, at a mixture ratio of 11 lb. of air to 1 lb. of fuel, the same gasoline was equal in knocking tendency to a reference fuel of 74 octane number. Both gasolines knocked more at lean mixture ratios, but starting from a rich mixture of 11 to 1, the knock increased more rapidly with the reference fuels as the mixture was made leaner, until a maximum was reached at about 14 to 1.

Fig. 3 shows the effect of speed changes upon the relative knock ratings of the same fuels, while mixture ratio is maintained constant at approximately 14 to 1. At 600 r.p.m. gasoline A 1 was found to be equal to a reference fuel of 82 octane number, and at 1,500 r.p.m. to a reference fuel of 74 octane number. Both the test fuel and the reference fuels decreased in knocking tendency with increasing engine speed, as shown by the increasing compression ratio required for incipient knock; but the knock decreased more rapidly with the reference fuels.

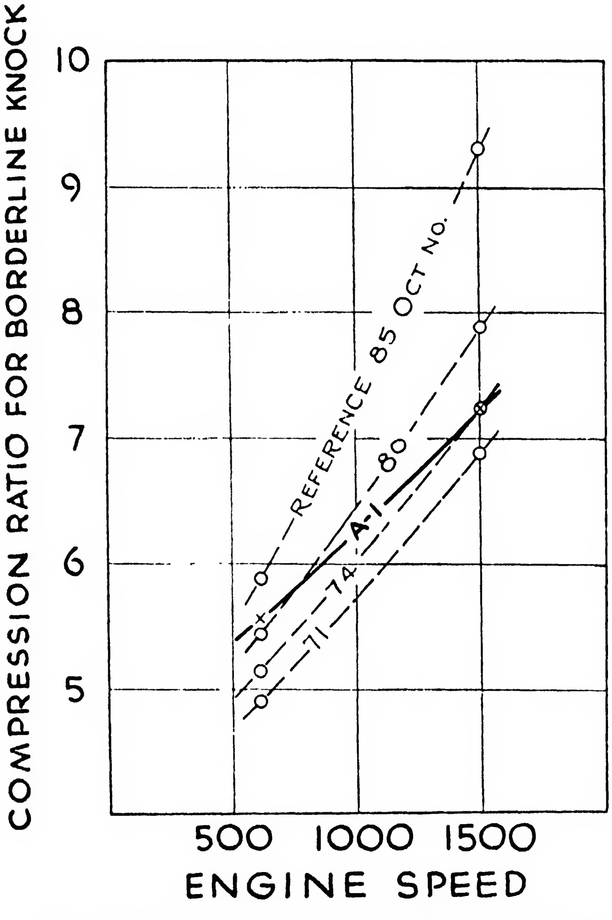


FIG. 3. Chart showing that, with fuels of different types, knocking tendency may be unequally affected by changes in engine speed. Single-cylinder, variable compression engine. Mixture ratio and spark for maximum power. Mixture 55–60° F. Jacket 212° F.

These data show why the knock rating of one gasoline with respect to another might be expected to vary over a range equivalent to several octane numbers with the large differences in conditions of engine operation that are commonly experienced in road tests. That such variations actually exist has been shown by a considerable amount of experimental work. An outstanding investigation of this kind was carried out in 1932 under the sponsorship of the Co-operative Fuel Research Committee. Representatives of 15 different laboratories representing the oil and automotive industries met at one place and determined representative road ratings of 15 different fuels as obtained in a number of different makes of automobiles [45, 1932; 47, 1933].

Some typical road ratings on one fuel included in this investigation are shown in Fig. 4. In this figure the vertical bars represent the spread in all ratings reported for each car, and the solid horizontal bars represent the average of what are sometimes called the maximum knock ratings on each car. The term maximum knock rating, as applied to a fuel, is the rating made at the point of highest degree of knock on that fuel in the car in which the rating is made. The procedure in which the ratings were thus made at this point of maximum knock in each car was agreed upon as giving the most significant road rating, and this procedure and the results obtained by means of it were used in all subsequent correlation work. The range in maximum knock ratings for the fuel reported in Fig. 4 was from 50 to 70% of 'C 6' in 'A 2' or the equivalent of about 5 octane numbers.

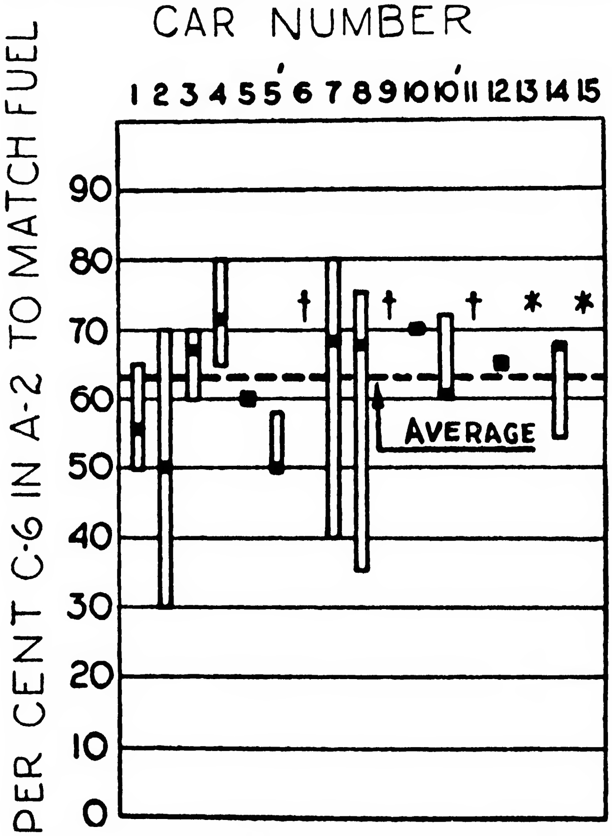


FIG. 4. Road knock ratings of one fuel in a number of different makes of cars. Data from 1932 Uniontown tests.

As a result of this extensive co-operative investigation the then current laboratory knock-testing procedure described above was modified to produce better correlation with the average ratings obtained in these road tests on 1932 cars. The modifications made in the original laboratory procedure were as follows:

1. Engine speed increased from 600 to 900 r.p.m.
2. Mixture temperature set at 300° F. (149° C.), the regulation being obtained by an electric heating element inserted between the carburettor and the engine.
3. Spark timing advanced to the following schedule:
    26 degrees before top centre at 5·0 : 1
    22 „ „ „ 6·0 : 1
    19 „ „ „ 7·0 : 1.

Features of the original procedure remaining unchanged were: bouncing-pin indicator and knockmeter as instrumentation, mixture ratio for maximum knock, and operation at wide-open throttle with water jacket at the temperature of boiling water.

The degree of correlation between ratings made by this modified laboratory procedure and the road ratings obtained in 1932 cars tested is shown in Fig. 5. Each road-test rating represented in this figure is an average of all road ratings obtained on that particular fuel. Of course, no one fuel was rated in all cars, because in some cars it either would not knock at all or it would knock too loudly to permit an accurate rating to be obtained. However, some of the fuels were rated in as many as 12 cars.

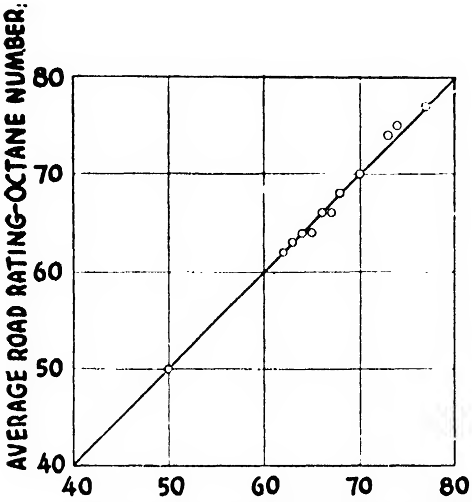


FIG. 5. Correlation between the average ratings obtained in road tests with 1932 American cars and laboratory ratings by A.S.T.M. Method D. 357–33 T, and I.P.T. Method G. 39 (T).

This modified knock-testing procedure, as thus developed by the Co-operative Fuel Research Committee, was then adopted by the American Society for Testing Materials and later by the Institution of Petroleum Technologists as a Tentative Method of Test for Knock Characteristics of Motor Fuels, current A.S.T.M. Designation D. 357–36 T, and I.P.T. Serial Designation G. 39 (T) [1, 1934–5]. It is the method now in general use for the determination of octane number. In accordance with the practice of the A.S.T.M. and the I.P.T., the method is subject to revision from time to time by general consent. Details of the procedure, embodying such revisions as may be made in it, are given in the current *Proceedings* of the American Society for Testing Materials [1*a*, 1934] and among the Standard Methods for Testing Petroleum and its Products of the Institution of Petroleum Technologists [1*b*, 1935]. The A.S.T.M. and I.P.T. procedures are identical except for the provision of a correction factor for ratings of benzol and alcohol blends in I.P.T. Method G. 39 (T).

The earlier knock-testing method using an engine speed of 600 r.p.m. and no heat on the mixture has since been known as the C.F.R. Research method and has been used for experimental purposes in conjunction with the present tentative standard A.S.T.M. method, for the determination of fuel 'sensitivity', or to study how much the knocking characteristics of fuels are affected by changes in engine conditions [45, 1932; 46, 1934; 47, 1933; 48, 1935].

In 1934 a second series of co-operative road tests or car correlation tests was made under the sponsorship of the Co-operative Fuel Research Committee. The correlation between ratings by the tentative standard A.S.T.M. method of test and the road tests on 1934 cars proved to be reasonably satisfactory, as shown by Fig. 6. Changes in the A.S.T.M. method may be expected, however, in keeping with whatever progress is made in this field. A more extensive discussion of the subject of road tests and of the correlation between the results of such tests and laboratory knock ratings is given in references [47, 1933] and [48, 1935], and in Article 16. Reference to chapter by R. Stansfield.

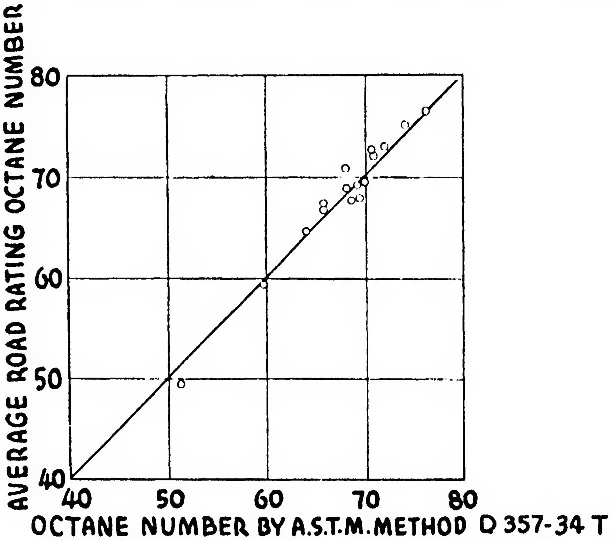


FIG. 6. Correlation between the average ratings obtained in road tests with 1934 American cars and laboratory ratings by A.S.T.M. Method D. 357–34 T, and I.P.T. Method G. 39 (T).

Reproducibility of Laboratory Ratings.

In 1932 5 samples of gasoline were rated in 11 different laboratories. The average deviation from the mean was 0·5 of an octane number, and the maximum deviation from the mean was 1·7 octane numbers [8, 1933]. In 1933 a more extensive test of reproducibility was made on a series of 10 samples of gasoline by 19 laboratories located in various parts of the United States [24, 1934]. The average deviation from the mean was about the same as found previously [8, 1933], but maximum deviations as high as 3 octane numbers were occasionally reported. Deviations of the order of magnitude of 3 octane numbers can usually be traced to lack of adequate control of test conditions, but occasional deviations of from 1 to 1½ octane numbers seem to be present even when every reasonable precaution is taken in making the tests. There is, therefore, a certain amount of experimental uncertainty about any one single knock rating. This observation has an important bearing upon ratings made directly against mixtures of heptane and *iso*-octane, such as might be made in cases of uncertainty. In such cases a single rating made even against these primary standards can hardly be considered absolutely valid within less than 1 octane number. A more dependable rating will be obtained by averaging several results obtained independently by a number of individuals.

Two factors which contribute to the reproducibility of results are: first, the adjustment of knock intensity, and, second, the making of a daily check of test conditions. In the earlier knock-testing procedure now known as the Research method, the knock intensity at which ratings were made was specified as one ratio above the point of incipient knock. Although this method of adjustment is given also in the present tentative A.S.T.M. method [1, 1934–5], it is useful only as a very rough approximation. It is necessarily approximate because the determination of the compression ratio for incipient knock depends somewhat upon the judgement of the observer. Several attempts have been made to provide a more satisfactory specification of knock intensity, but as yet none which is universally satisfactory has been found. One method which is widely used is to set the compression ratio at 5·3 to 1 and then, with a secondary reference fuel of 65 octane number, to so adjust the bouncing-pin contacts as to give a knockmeter reading of about 50. This adjustment should result in a clearance of from 0·003 to 0·005 in. between the bouncing-pin contact points. (The clearance volume of the combustion chamber, measured with oil or water, should be 142 c.c. at a compression ratio of 5·3 : 1.)

When the initial setting of the bouncing-pin has been made in this way, the compression ratio may then be adjusted to give approximately equivalent knockmeter readings on any particular fuel to be tested, and the bracketing with reference fuels may be carried out at that compression ratio. The data in Table II, which are representative for laboratories where the barometric pressure is between 28·50 and 30·50 in. of mercury, indicate approximately how the compression ratio may be expected to vary with octane number in accordance with this procedure. These data, which are an average obtained from a group of 19 different laboratories, are approximate because variations of plus or minus two- or three-tenths of a compression ratio were observed among different engines. Some of these variations appear to be characteristic of individual engines, and some to variations in barometric pressure.

TABLE II

Octane number	*Comp. ratio for rating by A.S.T.M. Method D. 357-34 T*
50	4·90
60	5·15
65	5·30
70	5·50
75	5·75
80	6·10

At the present time there is no very well-standardized practice for testing at high altitudes. However, individual organizations faced with this problem have usually worked out experimentally suitable modifications of the standard procedure to give reasonably satisfactory correlation with sea-level laboratories.

Another method which has been suggested for the adjustment of knock intensity is to set the knock intensity such that a mixture containing 65 parts by volume of *iso*-octane and 35 parts of normal heptane will be equal in knocking tendency to a mixture containing 68±1 parts by volume of benzene and 32∓1 parts of normal heptane. This test was originally developed as a means of checking the engine-test conditions; but it can also be used as a means of setting knock intensity in the sense that if the 65% *iso*-octane mixture is equivalent to 68% benzene in heptane, then test conditions, including knock intensity, may be assumed to be standard [1, 1934–5]. It is a common practice to use a blend containing 40–50% of benzene in a reference gasoline rated against secondary reference standards as a daily check on engine operation. This check serves as a means of making an initial bouncing-pin setting and of making sure that the equipment as a whole is in good operating condition.

In a co-operative investigation in which 3 commercial fuels were rated by 14 laboratories, no consistent differences in ratings were found among the three methods of adjusting knock intensity named above, i.e. (1) setting the compression one compression ratio above incipient knock, (2) setting the compression ratio at 5·3 : 1 for 65 octane number, (3) setting knock intensity so that 65% *iso*-octane in heptane is equivalent to 68% benzene in heptane. However, certain indications have been reported in which knock ratings of widely different types of fuel varied with knock intensity [43, 1934].

It is also well known that certain types of fuels of widely different compositions may give equal knockmeter readings and yet produce different degrees of knock intensity as judged by ear. Hence it is desirable to operate within reasonable limits of knock intensity in order that the bouncing-pin indicator may operate properly and produce results which on the whole correlate with average service tests. With either too light a knock or too heavy a knock, certain disturbing factors enter into the operation of the bouncing-pin and reduce its utility.

Two precautions in the way of operating technique that are important in connexion with reproducibility are: first, tests should be made occasionally to make sure that a given fuel will produce equal knockmeter readings on each one of the three carburettor float-bowls; second, sufficient time should be allowed to elapse after changing from one fuel to another for the new fuel to come to equilibrium knock intensity. The length of the time lag before equilibrium is reached may in extreme cases be from 5 to 10 minutes, but usually it is not so long as this [31, 1931].

Special Problems in Knock Testing

The A.S.T.M. knock-testing method was developed primarily as a test that would give results which are in general agreement with the average results of road tests of representative present-day motor fuels in current commercial passenger-car engines. The application of this method of test to fuels outside the range of commercial fuels either in knocking tendency or in chemical composition, or to engines widely different from current passenger-car engines, is open to question unless confirmed by service tests. Even among present-day passenger-car engines, exceptional cases will be found where exact correlation between laboratory ratings and service ratings of widely different types of fuels is lacking. The existence of these exceptional cases has caused a considerable amount of attention to be given to the causes of these exceptions. As was pointed out early in this article, knock ratings of one type of fuel with respect to another and widely different type of fuel may vary with engine conditions. Accordingly, where knock ratings made in service in different cars cover a range of car speeds between 15 and 50 m.p.h., as well as a range of mixture ratios, spark timings, and mixture temperatures, about the most that can be expected of a rating by any one method of test, such as the present tentative standard A.S.T.M. method, is correlation with *average* service ratings. Individual departures from correlation among extreme types of fuels in certain individual cars amounting to as much as 4 or 5 octane numbers may sometimes be observed.

The fact that different types of fuels which contain high proportions of unsaturated or aromatic hydrocarbons, as distinguished from gasolines which are highly paraffinic or naphthenic, show different degrees of response in knocking tendency to engine variables has made it desirable to have some measure of these differences between fuels. One measure of this 'sensitivity' to changes in engine conditions has been obtained by comparison of the knock ratings obtained by the original C.F.R. Research method [6, 1931] with those obtained by the tentative standard A.S.T.M. method [1, 1934–5]. This comparison offers a convenient and useful means of obtaining a measure of fuel 'sensitivity' with respect to mixtures of *iso*-octane and heptane, even though it is subject to certain limitations. One of these limitations is that it does not provide for any differentiation in 'sensitivity' according to separate engine variables, i.e. as to whether the fuel is most sensitive to changes in speed, to variations in mixture temperature, or to changes in other operating conditions. However, the data of the co-operative road tests made in 1934 [48, 1935] indicate that, in spite of the lack of differentiation between engine variables which is inherent in a comparison of ratings made in the laboratory by the Research method with those obtained by the tentative standard A.S.T.M. method, those fuels which were 'sensitive' with respect to the reference fuels by the laboratory tests were also 'sensitive' with respect to the same reference fuels in actual service tests. Another limitation is that the comparison measures 'sensitivity' with respect to heptane and *iso*-octane mixtures, and implies that the heptane and *iso*-octane mixtures do not change and that the changes observed are entirely with the fuel which is rated against these two reference fuels. This implication is not strictly true, since the knocking tendencies of all fuels are affected by changes in certain engine conditions. Accordingly, in measuring 'sensitivity' by this means it should be recognized that the results are relative to the reference fuels and are not absolute in the sense that they are independent of the reference fuels used as a basis for comparison.

Measurement of knocking tendency directly and irrespective of reference fuels, as was done in the technique employed in obtaining the data represented in Figs. 2 and 3, is thus sometimes advantageous in obtaining a clear mental conception of knocking behaviour. Some of the advantages of this method for experimental investigations are: first, that knock ratings are expressed in terms of a tangible concept, compression ratio, that is widely held among engineers; second, that it can be used to follow the behaviour of widely different types of fuels irrespective of reference fuels; and, third, that it can be made to cover a wide range of fuels. (The disadvantages of this method which make it unsuitable for a general knock-testing procedure were cited earlier in this article.) Incidentally, there are some indications that equal increments of compression ratio are equivalent to approximately equal increments of knock intensity on any part of the compression ratio scale between 3 to 1 and 15 to 1 [29, 1934]. That this is not true of the octane number scale is shown by the data in Fig. 7, which is a plot of compression ratio for incipient or just audible knock against per cent. of *iso*-octane in normal heptane in the C.F.R. test engine when operated in accordance with the test conditions specified in A.S.T.M. Method D. 357–34 T. This chart shows how the increment in anti-knock value per unit change in octane number increases more rapidly between 70 and 100 octane number than it does below 70 octane number. For example, a 10 octane number change between 80 and 90 octane number is equal to a difference of 0·60 of a compression ratio, whereas 10 octane numbers between 50 and 60 is equivalent in anti-knock effect to only about 0·25 of a compression ratio. This figure also shows the comparatively narrow range of knocking tendencies represented by present-day motor gasolines.

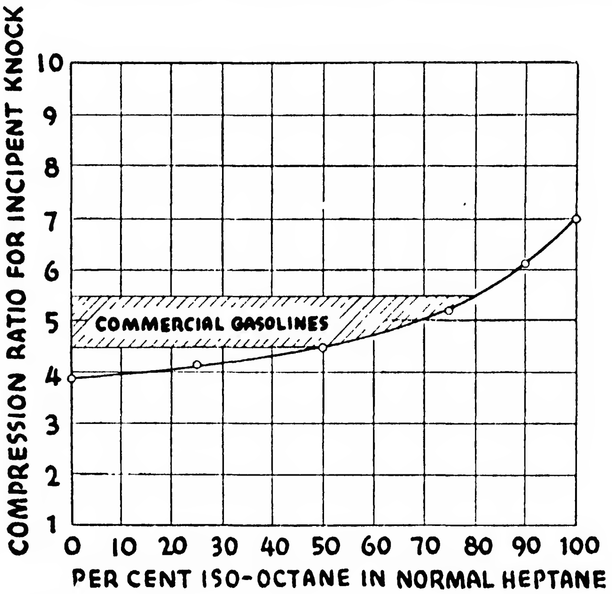


FIG. 7. Approximate relationship between octane number and compression ratio for incipient knock. Engine operated in accordance with engine conditions specified for A.S.T.M. Method D. 357–34 T, and I.P.T. Method G. 39 (T).

PART II. AVIATION FUELS

General Considerations.

In rating aviation fuels for knock, the tendency of the fuel to heat the cylinder and the piston is generally accepted as a more important criterion of the suitability of a fuel than the tendency to emit audible sounds recognized as knock [22, 1930; 35, 1930]. In aircraft engines the operating temperatures reached by the parts forming the combustion chamber are at times not far below the limits for safety even with the best of fuels, and so a tendency on the part of any particular fuel to cause excessive heating is undesirable and can lead to rapid mechanical destruction of the engine. There is also evidence that the relative tendencies of different fuels to heat the combustion-chamber walls are not always in accord with their tendencies to produce audible knock [22, 1930]. For these reasons, service tests made on aviation fuels at the present time are usually based on temperature measurements on some part of the combustion chamber rather than on records of audible knock such as have been used in testing automobile fuels.

Some typical aircraft-engine data depicting the aviation fuel problem as observed in actual service are given in

Fig. 8. This figure is a reproduction of some data given by Gagg and Losson [19] in a report presented at the World Petroleum Congress in London in 1933. The figure shows maximum cylinder-head temperatures and brake horse-power for various fuels plotted against rate of fuel consumption at constant speed and full throttle. These data indicate the characteristic tendency of the cylinder-wall temperature to rise with all fuels as the fuel flow rate approaches maximum economy. At the same time, after the mixture ratio is made leaner than that for maximum power, certain individual fuels have a tendency to produce a sharp rise in temperature which is usually accompanied by knocking. It is this tendency to produce this distinctively sharp rise in temperature that determines the relative suitability of different fuels in an aircraft engine. This is because, if this type of rising temperature is not checked either by throttling or by enriching the mixture, it tends to produce a cumulative increase in temperature resulting in rapid destruction of the engine.

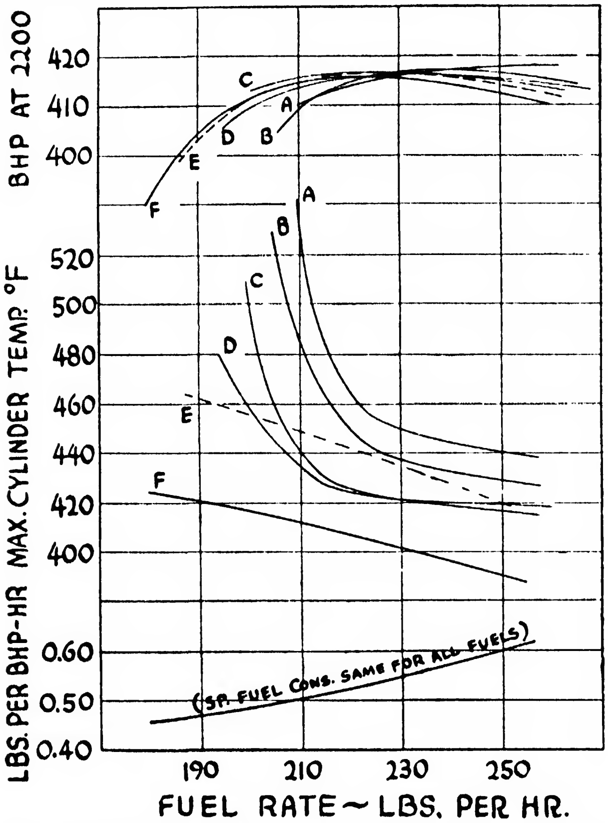


Fig. 8. Comparative tests of several fuels. Wright whirlwind engine model R. 975 E. Compression ratio 6·0:1, blower 10·15:1.

The problem of rating aviation fuels correctly in a small-scale laboratory test-engine becomes, therefore, a matter of finding a means of rating fuels in order of their heating tendencies in full-scale engines. It is to be noted that in this respect the term 'knock' rating as applied to aviation fuels has a special meaning and does not necessarily bear any relation to audible knock in the commonly accepted sense. Incidentally, it might be mentioned also that of the fuels shown in Fig. 8, all but fuel *F* had knock ratings of 80 octane number by a now obsolete method of test. Fuel *F* had a rating of 87 octane number. All of these fuels were suitable for this engine under certain conditions, but fuels *A*, *B*, and *C* would require careful control of the throttle and mixture ratio in order to avoid engine failure.

Laboratory Rating of Aviation Fuels.

At the present time several laboratory methods of test are being used for rating fuels in order of their suitability, i.e. 'knock' ratings, for aircraft engines. In America commercial aviation fuels are being rated by the current A.S.T.M. Method D. 357–34 T [1, 1934–5], already described in connexion with automobile fuel testing. This method has been recommended by the Aviation Gasoline Detonation Sub-committee of the Co-operative Fuel Research Committee pending the development, now in progress, of a more thoroughly tested procedure. Experience has shown that this method gives a reasonable degree of correlation with service tests without departing from already standardized equipment and practice [14, 1933]. Since it was thought, however, that this method would give too favourable ratings on certain types of fuels such as benzol blends, alcohol blends, and some cracked gasolines, the sub-committee has recommended that definite octane ratings be applied only to commercial aviation fuels which meet the following specifications:

1. A freezing-point of not more than −60° C. (−76° F.).
2. An acid heat of not more than 20° F. with C.P. sulphuric acid of 1·83–1·84 specific gravity.

Another test which is now in use is that of the United States Army Air Corps (Air Corps Spec. No. 3566 A). The engine used in this test is a modified C.F.R.-A.S.T.M. engine. The principal modifications comprise a special cylinder having a $2\frac{5}{8}$-in. bore, a sodium-cooled, stellite-faced exhaust valve, removal of the intake mixture heater, and operation with di-ethylene glycol as a cooling liquid at a jacket temperature of 330° F. The engine is operated at 1,200 r.p.m., and fuels are rated on the basis of the temperatures indicated by a thermocouple placed in a 'temperature plug' which is screwed into a tapped hole in the cylinder head. The construction of this temperature plug is shown in Fig. 9.

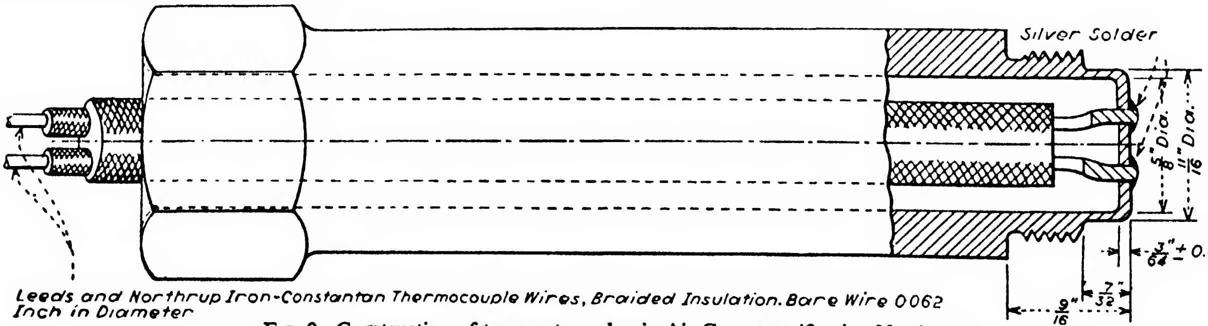


Fig. 9. Construction of temperature plug in Air Corps specification No. 3566 A.

In carrying out this method of test, fuels are matched on the basis of observed temperature-plug readings, rather than on the basis of knock intensity. A 'standard plug temperature' is first established. This temperature is that obtained when the compression ratio is adjusted to give the same temperature with 88% *iso*-octane in heptane as with C.P. benzene, the carburettor having been adjusted previously to produce maximum temperature obtainable with each fuel. The test fuel is then compared with *iso*-octane in heptane at the compression ratio at which the test fuel produces 'standard plug temperature' at the carburettor setting for maximum temperature. The octane number of the test fuel is then defined as being equal to the per cent. *iso*-octane in the mixture of *iso*-octane in heptane which matches this temperature at this compression ratio. Particular attention is given in the test to the detection of a tendency towards pre-ignition. If the engine fails to produce a clean cutting-out on the test fuel when the ignition is shut off during the above test, the compression ratio is progressively lowered until this evidence of pre-ignition just ceases. The octane number is then determined at this compression ratio and is defined as equal to the per cent. *iso*-octane in the *iso*-octane-heptane blend which produces 'standard plug temperature' at this reduced compression ratio, irrespective of the temperature produced by the test fuel under these conditions.

In England the I.P.T. has recommended the current method for automobile fuels modified to the extent of changing the mixture temperature from 300° to 260° F. (I.P.T. Serial Designation G. 38*a* (T) [37*a*, 1933; 37*b*, 1935]). This change was based on tests by audible knock of 9 different fuels in 2 full-sized, single-cylinder aircraft engines, 1 water cooled and 1 air cooled. It was found that a mixture temperature of 260° F. for the C.F.R. laboratory testing engine produced results in good agreement with ratings obtained on the full-sized engines for fuels of not above 80 octane number.

Further developments and more universal standardization of methods of rating aviation fuels are to be expected as knowledge in this field increases. At the time of writing the current methods of rating aviation fuels are considered to be in the development stage. The recent introduction of *iso*-octane as an aviation fuel [26, 1935] and of *iso*-octane plus lead tetraethyl, making commercial fuels higher than 100 octane number [12, 1935], has introduced new elements into the picture which have not yet been adequately provided for in knock-rating technique.

The authors wish to acknowledge the assistance of S. D. Heron of the Ethyl Gasoline Corporation, Detroit, Michigan, in the preparation of Part II.

REFERENCES

1. (*a*) American Society for Testing Materials, *Tentative Standards*, 611 (1934).
   (*b*) Institution of Petroleum Technologists, *Standard Methods*, 3rd ed., 210 (1935).
2. Becker, A. E., and Kass, C. B. *Proc. World Petr. Cong.* **2**, 150 (1933).
3. Berl, E., Heise, K., and Winnacker, K. *Chaleur et Ind.* **10**, 179 (1929).
4. Boyd, T. A. *Bull. Amer. Petr. Inst.* **8**, 193 (1927).
5. —— *Bull. Amer. Petr. Inst.* **11**, sect. iii. 38 (1930).
6. —— *Bull. Amer. Petr. Inst.* **12**, sect. iii. 46 (1931).
7. —— *Proc. Second Mid-year Meeting, Amer. Petr. Inst.* 98 (1932).
8. Boyd, T. A., and Veal, C. B. *Proc. World Petr. Cong.* **2**, 139 (1933).
9. Brooks, D. B., White, N. R., and Rogers, G. C. *J.S.A.E.* **29**, 45 (1931).
10. Brown, G. G. *Bull. Amer. Petr. Inst.* **8**, 191 (1927).
11. Campbell, J. M., Lovell, W. G., and Boyd, T. A. *J.S.A.E.* **29**, 129 (1931).
12. Cronstedt, V., DuBois, R. N., Klein, F. D., and Heron, S. D. *J. Aeronautical Sciences*, **2**, 125 (1935).
13. Cummings, H. K. *J.S.A.E.* **20**, 605 (1927).
14. —— *Proc. World Petr. Cong.* **2**, 193 (1933).
15. Edgar, Graham. *Ind. Eng. Chem.* **19**, 145 (1927).
16. —— *J.S.A.E.* **29**, 52 (1931).
17. Egerton, A., and Gates, S. F. *J.I.P.T.* **13**, 273 (1927).
18. Egloff, Gustav, and Morrell, J. C. *Ind. Eng. Chem.* **18**, 354 (1926).
19. Gagg, R. F., and Losson, W. L. *Proc. World Petr. Cong.* **2**, 198 (1933).
20. Garner, F. H., and Dodds, E. M. *Engineering*, **134**, 45 and 60 (1932).
21. Heron, S. D. *A.S.M.E. Trans.* **52**, part i. 233 (1930).
22. —— *J.S.A.E.* **28**, 694 (1930).
23. Huf, H. F., Sabina, J. R., and Hill, J. B. *J.S.A.E.* **29**, 134 (1931).
24. —— —— —— *Oil and Gas J.* **32**, no. 40, 20, 43 (1934).
25. King, R. O., and Moss, H. *Engineering*, **128**, 219, 272 (1929).
26. Klein, F. D. *J. Aeronautical Sciences*, **2**, 43 (1935).
27. Lee, S. M., and Sparrow, S. W. *J.S.A.E.* **12**, 11 (1923).
28. Leslie, E. H., Brown, G. G., and Hunn, J. V. *Ind. Eng. Chem.* **17**, 397 (1925).
29. Lovell, W. G., Campbell, J. M., and Boyd, T. A. *Ind. Eng. Chem.* **26**, 1105 (1934).
30. MacCoull, Neil. *J.S.A.E.* **22**, 457 (1928).
31. —— *J.S.A.E.* **29**, 193 (1931).
32. Masson, H. J., and Hamilton, W. F. *Ind. Eng. Chem.* **19**, 1335 (1927).
33. —— —— *Ind. Eng. Chem.* **20**, 813 (1928).
34. Midgley, Thomas, and Boyd, T. A. *J.S.A.E.* **10**, 7 (1922).
35. Parkins, W. A. *J.S.A.E.* **28**, 679 (1930).
36. Peletier, L. A. *Proc. World Petr. Cong.* **2**, 165 (1933).
37. (*a*) Pye, D. R. *Proc. World Petr. Cong.* **2**, 186 (1933).
    (*b*) Institution of Petroleum Technologists, *Standard Methods*, 3rd ed., 218 (1935).
38. Ricardo, H. R. *Auto. Eng.* **11**, 51, 92, and 130 (1921).
39. Roesch, Daniel. *J.S.A.E.* **19**, 17 (1926).
40. Sims, C. J., and Mardles, E. W. J. *Report British Air Ministry* (1926).
41. Stansfield, R., and Carpenier, R. E. H. *J.I.P.T.* **18**, 513 (1932).
42. Stansfield, R., and Thole, F. B. *Ind. Eng. Chem.*, Anal. Ed. **1**, 98 (1929).
43. Taylor, C. F., Draper, C. S., Taylor, E. S., and Williams, G. L. *J.S.A.E.* **34**, 59 (1934).
44. Tizard, H. T., and Pye, D. R. *Phil. Mag.* **44**, 79 (1922).
45. Veal, C. B., Best, H. W., Campbell, J. M., and Holaday, W. M. *Bull. Amer. Petr. Inst.*, sect. iii. 139 (1932).
46. Veal, C. B. *Bull. Amer. Petr. Inst.* **15**, sect. iii. 38 (1934).
47. Veal, C. B., Best, H. W., Campbell, J. M., and Holaday, W. M. *J.S.A.E.* **32**, 105 (1933).
48. Veal, C. B. *J.S.A.E.* **36**, 165 (1935).
49. Wilson, R. E. *Bull. Amer. Petr. Inst.* **8**, 192 (1927).

16. THE CORRELATION OF ROAD AND LABORATORY KNOCK RATINGS OF MOTOR FUELS

By R. STANSFIELD, A.M.Inst.C.E., M.Inst.P.T.

Anglo-Iranian Oil Company, Ltd.

Limitations to Complete Correlation between Service Ratings and Laboratory Ratings of Anti-Knock Value of Fuels.

EARLY attempts to correlate service data regarding the relative knocking tendencies of gasolines and measurements of anti-knock value in the laboratory were largely based on inadequate service data and have little present-day value.

They were frequently carried out only on a limited number of fuel samples of special interest to the particular company making the tests; the number of cars or other engines on which these were tested was extremely small; the range of engine sizes was often too restricted, and no standard laboratory test engine existed by which the findings of one laboratory could be compared with those of another.

Under these conditions it was found possible to make results from almost any laboratory test correlate with the service data within reasonable limits, serious divergencies appearing only when the range of gasoline types was extended by the increasing use of cracked and leaded fuels, and when service data obtained mainly from large engines was compared with data from much smaller units.

Starting with the Co-operative Fuel Research engine as the laboratory test unit, and expressing the anti-knock ratings from this engine in terms of octane numbers or any other repeatable reference system, it is usually possible to select test conditions which grade any number of fuels in the same relative order with regard to knock as obtained by service tests on any one type of car engine.

Such correlation between one set of laboratory conditions on the C.F.R. engine and the behaviour of one particular engine in service should be possible, in the majority of cases, to an accuracy of the order of two or three octane numbers, and may become the basis for an engine 'severity factor' to which reference will be made later.

It is found, however, that if engines of different makes, sizes, or types are tested on a series of fuels, or even when engines of the same make and size are compared under conditions permitting of the normal differences due to adjustments, carbon deposits, &c., that close correlation becomes impossible.

The actual methods used for service tests will be considered in detail below, but, assuming a suitable method to be available, the spread of results from service tests of engines on the road is indicated by the following figures taken from the 1934 Uniontown Tests (Veal [1, 1934]). The fuel number is given in the first column, the fuel types covering a wide range chemically, and including straight-run, cracked, and leaded gasolines. The road ratings converted to octane number equivalents are given for two different cars in columns 2 and 3. Column 4 gives the differences between the cars as regards observed ratings.

It will be noticed that the ratings from the second car selected for the above example vary from zero to ten octane numbers from the first car's ratings. We are thus faced with the problem of deciding how the laboratory engine shall be adjusted. If it agrees with either of the above examples, it will give results in error up to as much as ten octane numbers for the other car. It is clear that the only reasonable solution of this problem is to take average road ratings, and not only the average of two or three service types, but of as many as can be tested with as wide a fuel type range as possible. Further, the service type engines should be selected, since some selection is unavoidable, so that the range is typical of the general distribution on the road, and proportioned to the gasoline consumption of the various sizes.

TABLE I

	2	3	
1	*Equivalent o. nos.*		4
Fuel	*Car 2*	*Car 19*	*Diff.*
1	70	67	3
3	78	74	4
4	59	57	2
6	68	68	0
13	68	66	2
16	70	67	3
12	76	66	10
5	67	62	5
10	67	62	5
8	64	60	4
2	73	68	5
9	70	66	4
11	77	72	5
7	73	66	7
15	73	72	1

The correlation problem is thus reduced to obtaining the averages of knock ratings in service for a wide range of fuels and engines, and then to the determination of C.F.R. conditions which give the best agreement with these averages.

It is inevitable, from the nature of such ratings, that laboratory ratings cannot be expected to agree exactly with any service type of engine. They may agree within one or two numbers with some types and they may differ by as much as ten numbers from others. The differences may be either positive or negative in sign—they are not indicative of bad laboratory correlation, but represent actual differences between the behaviour of different engines in service and must be accepted as such.

Use of the results only from one or two engines to show a particular set of laboratory engine conditions to be good or bad is illogical and indicates a lack of appreciation of the factors involved.

Another difficulty, particularly affecting international standardization, arises from the different distribution of engine sizes and fuels in different countries.

About 75% of gasoline sold in the U.S.A. (other than for aviation) is used by private cars and only about 25% for commercial vehicles. The commercial vehicles, as a class, have engines of average size and type very similar to the private car engines, the weighting to allow for the larger trucks being only small. In Great Britain only about 35%

of the gasoline is used by private cars for engines averaging about 12 H.P. (R.A.C. Rating) and about 65% is used for lorries. The average size of the latter is about 21 H.P. While the price differential between the lower and higher octane number grades tends to divide the gasolines on the market between commercial and private cars (the engines themselves being designed to suit the different octane numbers) there is considerable overlapping, and it is obvious that it would be impracticable to have one type of C.F.R. test for low octane number fuels and another for the higher octane numbers. This means that road tests made for correlation purposes for the British market should include a preponderance of commercial (the larger cylinder capacity) engines in the proportion of about 70% to 30% of the smaller sizes, these figures allowing for the fuel consumptions of the two classes. Such tests have never been made, but, fortunately, the U.S.A. test results can be applied with some confidence since the average size of the engines used corresponds very well with what is required.

The greater range of cylinder sizes used in Great Britain for all purposes taken together means that individual ratings will vary more from the mean laboratory ratings than will be the case for U.S.A. correlation, so that even a 10 octane number deviation may be exceeded in certain combinations of cars and fuels.

The position in other countries needs to be examined in a similar manner with full recognition of the importance of securing a fair average of engine types. Any final correlation is unlikely to be much different from that suitable for America and Britain, but progress towards international agreement is seriously hindered by lack of appreciation of the fact that the laboratory figures are intended to serve as a guide for the oil producers to enable them to blend to suitable octane numbers, and that they can never, no matter what the technique, replace individual road tests which may be required to determine the special behaviour of a particular engine type on a particular fuel or fuels.

The Uniontown Tests of 1932, and the Motor Method

The first organized co-operative road tests were arranged by the C.F.R. Committee and took place at Uniontown, Pennsylvania, in 1932. At this time the C.F.R. engine was distributed through the more important American laboratories and had been used under conditions now known as the 'Research Method', which included running at the low speed of 600 r.p.m. with unheated mixture. It is now apparent that such conditions, coupled with the use of an engine having the cylinder cast integral with the head, were not representative of knocking conditions existing in current private vehicles. The low speed meant that valve and combustion chamber wall temperatures remained low, and the unheated mixture was not typical of any usable car engine, for, without greater heating than was adopted for the Research Method, good acceleration would be almost impossible in an average design. Special designs might operate with cold mixture, but to judge from these was to overlook an axiom of correlation—that it must be a correlation with an average type of engine. The use of evaporative cooling in an integral cast head was not more severe than normal cooling with an outlet temperature of, say, 170° F. in an engine with a detachable head and of usual design.

It is not surprising that the first Uniontown tests showed that the Research Method conditions were in poor agreement with road averages.

Laboratory work following the 1932 tests resulted in the adoption, as a tentative standard, of the 'Motor Method' of test on the C.F.R. engine. The engine was speeded up to 900 r.p.m., the mixture was heated to 300° F., and other minor changes were made. It should be noted that this speed is still below that at which most of the objectionable knock occurs in service tests on the road, and, remembering also the good cooling qualities of the integral head of the C.F.R. engine and the fact that it is distinctly of better thermal design than the average vehicle engine, the need for a mixture temperature of 300° F. becomes understandable. Mixture temperatures measured in vehicle manifolds vary from about 80° F. to about 150° F. with an average of about 120° F. Possibly the entire rise to 300° F. used in the laboratory engine may not be justifiable, but it does not seem probable that a temperature lower than 200° F. as a minimum can be adopted, and, if this is conceded, there is little to be gained from any departure from the Motor Method, since the result of such a small change only leads to a general rise of octane numbers without favouring or punishing any one fuel type by an amount sufficient to be of importance.

Methods of making Road Tests.

It has been emphasized that the object of road tests is to obtain data from each of several cars on a suitable series of fuels so that the average results from all the cars may be taken on which to base laboratory correlation, but nothing has been mentioned of the method by which the road results themselves should be derived (Veal [1, 1934]).

Fig. 1 is a graph showing to an arbitrary scale the knock intensity of an engine on the road plotted against the speed in m.p.h. during acceleration on full throttle from 15 to 60 m.p.h. The results for eight fuels are given, and it is clear that almost any method of rating will put these fuels in the same relative order. If, on the same car and under the same conditions, standard fuels of low and high octane number are blended in various proportions (dotted curves) and tested, it is possible to obtain ratings in terms of these road standards. Laboratory tests may then be made to find

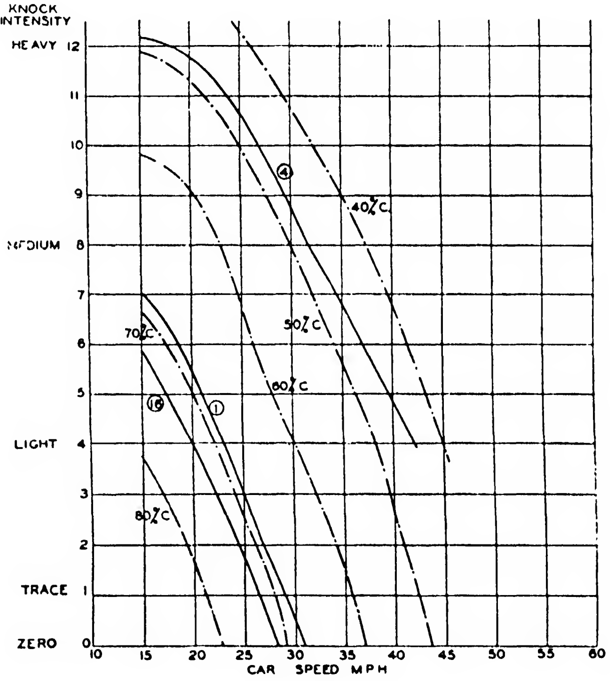


Fig. 1.

the C.F.R. engine conditions which make each of the test fuels match the appropriate blend of standards.

The fuel marked '1' in Fig. 1 starts with a moderate knock at 15 m.p.h. and falls to zero knock at 31 m.p.h. It is very slightly worse than the blend of reference standards containing 70% of the higher octane number reference fuel used (shown by the 70 dotted line), but considerably better than the 60% blend of standards. Inspection shows it to be equal, on the car selected, to approximately a 60% blend of the reference fuels. Fuel 4 equals a 48% blend of reference fuels, while fuel 16 equals a 73% blend. In this particular case it is immaterial whether the rating is made in terms of the relative maximum knock intensities at the beginning of acceleration, or the average intensity during acceleration ('knock integral') or the speed at which knock is extinguished on the rising speed. The tests might be made on a decelerating run up a hill of sufficient gradient without material alteration to the results—the absolute values of the intensities might change by the alteration in test technique, but the relative results would remain the same.

Such data is easy to interpret and no possible errors of judgement arise on account of the technician's special way of dealing with his work.

When cases occur such as those shown in Figs. 2 and 3 —cases which are not uncommon in practice—it becomes very important to consider how far any technically suitable method of measuring the knock can be assumed to give values which really correspond to the average user's judgement of the fuels.

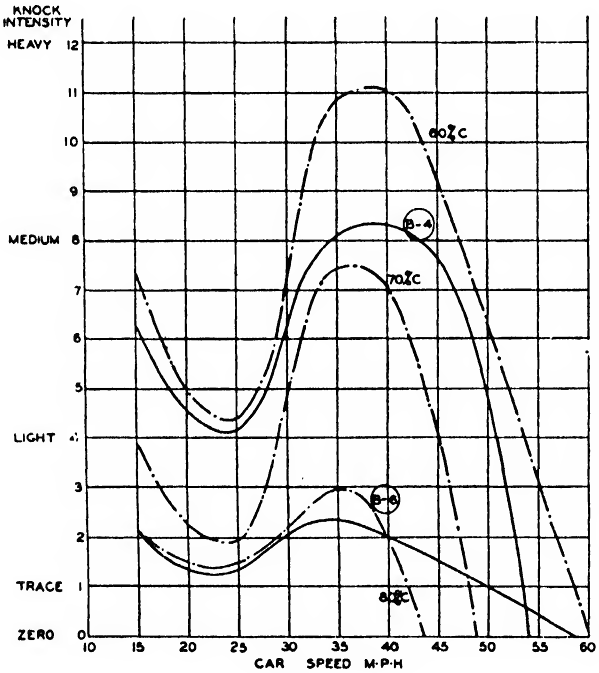


FIG. 2.

Until the 1932 Uniontown tests most road knock ratings were based on the relative speeds at which knock was extinguished as the car accelerated on full throttle, or on the relative speeds at which it appeared on deceleration uphill. As a technician's method of rating this procedure is simple and, under suitable conditions, repeatable. A glance at Fig. 2 shows how far it may mislead. Fuel *B*-6 in this figure reaches knock extinction at 58 m.p.h. and fuel *B*-4 reaches extinction at 54 m.p.h. Reference fuel 70 (dotted) gives no knock beyond 48 m.p.h. Fuel *B*-6, however, never knocks really heavily throughout the speed range, while *B*-4 and 70 *C* both reach fairly high intensities between 30 and 40 m.p.h.

It will be agreed that most ordinary drivers would prefer the rather prolonged but very mild knock of fuel *B*-6 to the heavy, although abruptly falling, knock of fuels *B*-4 and 70 *C* during the middle speed range.

Considerations of this sort led the C.F.R. Committee to the decision that the better method for the technical rating of fuels on the road was to grade the fuels tested in terms of relative maximum knock intensity, or in terms of the blends of reference fuels which gave the same maximum knock intensity as the samples under test, irrespective of the speed at which maximum knock occurred. This method of rating, complicated as it always appears to any one who has not attempted to use it, is not a difficult one, and the curves obtained by plotting intensities against speed range give an extremely useful record of fuel behaviour and engine idiosyncrasies.

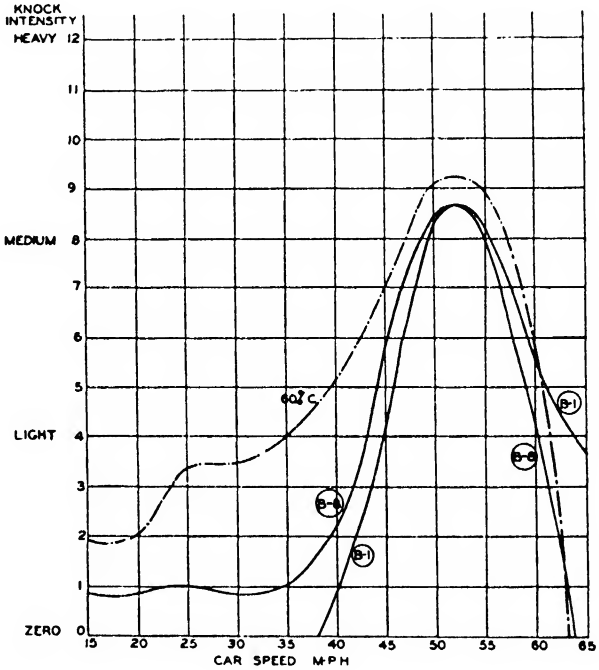


FIG. 3.

The curves of Fig. 3 show, however, that even this method cannot be an infallible guide to users' opinions, and unless the average user's opinions are obtained the method is open to criticism. Fuel *B*-1 in Fig. 3 does not knock at all until a speed of 38 m.p.h. is reached, after which the knock rises to a maximum at 52 m.p.h. and has not disappeared at 70 m.p.h. Fuel *B*-8 reaches the same maximum at 52 m.p.h. with extinction at 64 m.p.h., while fuel 60 (dotted) rises to a higher maximum, but falls to zero at 63 m.p.h.

Driving mainly in town traffic, a user would consider fuels *B*-8 and 60 to be much worse than fuel *B*-1. In the open country he would accelerate rapidly through the lower speed range and might consider fuel *B*-1 the worst. The C.F.R. method of rating grades *B*-8 and *B*-1 the same for this test, and 60 is graded only about 1½ octane numbers worse.

As part of an attempt to make the analysis of the 1934 Uniontown test results more complete, figures are given later for average ratings from many cars based on the official method (maximum knock), on the older method by which ratings were taken from relative speeds for knock extinction, and on an additional method depending on an inspection of the areas under the intensity curves (the 'knock integral'). The last method allows as far as possible for the probable average effect on the user of a combination of car and fuel which shows abnormal characteristics such as knock only at high speeds, double peaks in the knock curve, rapidly falling as compared with slowly falling knock, &c. It is admittedly only a first approximation, but is probably as accurate, if not more accurate, than the other methods, and any personal error of interpretation of one curve will be cancelled by errors in the opposite direction for other curves for the same fuel on other cars.

This threefold analysis has the added advantage of showing very clearly that road ratings vary somewhat according to the rules laid down for their determination. The rules, in turn, depend upon some agreed interpretation of a variable human factor and so, in final analysis, road ratings involve a certain factor of human judgement. This is why it is doubtful, in the present state of the art, whether the use of sound-measuring apparatus would make the ratings any more significant than those obtained with the unaided ear.

The Use of Reference Standards for Road and Laboratory Tests

An already complicated problem is still further confused by the use of reference standards, although it is difficult to suggest a better alternative.

In order to refer road results as easily as possible to laboratory figures, the road tests were made against blends of two reference fuels, the lower having a Motor Method octane number of about 44 and the higher a number of about 77. Blends differing from each other by 10% of the higher octane number fuel were tested in each car so that the curves obtained for samples could be compared with a range of curves from the reference blends selected to cover maximum knock intensities from the least discernible to the heaviest. It will be noted (Fig. 2) that one of the samples gave a curve which cut through the curves for the reference fuels in the higher speed range, and, in fact, it was known that the reference fuels selected were the nearest suitable obtainable approach to octane/heptane standards. Had reference fuels been chosen which were more nearly the same in character as the average of all the test samples, the curves from them would have been intermediate between those samples approximating to octane/heptane blends in nature and those of the 100% cracked gasoline or the rich benzole blend, and the actual ratings on the maximum knock basis would have been different in a few cases. The differences would not, however, have had much effect on the final averages or the proper conditions for laboratory correlation.

The use of a high octane reference fuel intermediate between the naphthenic *C* fuel and benzole would have been more representative of the average of the fuel samples, and this type should receive consideration for future road tests, although it would introduce the need for C.F.R. calibrations against octane/heptane over a wide range of mixture temperatures for the correct laboratory correlation conditions to be determined.

1934 Uniontown Road Test Results and Correlation with Motor Method and other C.F.R. Ratings

It is desirable to summarize the points which must be remembered when interpreting the 1934 test results which follow.

(*a*) The correlation of road and laboratory tests is not a correlation of results from one or two types of car or one or two types of fuel with laboratory figures, but an attempt to correlate the average results obtained from each of a large number of fuels on a large number of cars selected to give a true average of fuel and car types in use.

(*b*) The laboratory method adopted applies to present conditions and may have to be altered as car engine design changes. Any standardization is, therefore, only tentative.

(*c*) The method of interpreting the road test results is one adopted as suitable for obtaining numerical values. In addition to the C.F.R. official method two other methods have been used below. Any of the three methods can, in appropriate circumstances, be justified as the most suitable, the maximum knock method and the method depending on examination of the areas under the knock curves being the most useful for indicating the views of users. Neither the official nor any other method should be considered as infallible, and study of the differences between the various methods emphasizes the approximate nature of any correlation, and therefore points to the futility of criticism based on individual results.

(*d*) The experimental error of road tests appears to be of the order of 4 octane numbers for a given test. This is an extreme value and the usual error is probably much smaller. The maximum error of the averages for any fuel based on tests on all the cars is of the order of 2 octane numbers, but this error is unlikely to apply to more than one or two fuels, and there is no indication of its direction except in 2 cases where the samples approximated to the reference fuels in type.

(*e*) The official ratings are based on test results which had to be repeated to within approximately 3 octane numbers relative rating by an independent group of observers. A total of 653 hill ratings was made, and less than 7% of these had to be discarded as outside the permissible limits. In 6 cases only, where check ratings came outside the 3 octane number range allowed, the average of 3 ratings was taken, the range of the 3 ratings not exceeding 5 octane numbers. While these ranges appear large, the inclusion or rejection of such ratings has no appreciable effect on the grand averages.

(*f*) The ratings based on knock extinction speeds are determined from the curves of knock intensity for each car by plotting the speeds at which knock disappeared, or at which it reached a suitable low value, against the laboratory octane numbers. A smooth curve was then drawn to pass equally among the plotted points. The deviation in octane numbers was then measured as the deviation of each fuel rating point from the mean curve.

After determining the deviation for each fuel on each car for which data was available, the algebraic average deviation was calculated and the values obtained plotted against the C.F.R. test figures to indicate the correlation obtained with various methods of laboratory test.

(*g*) The ratings based on the general nature of the plotted curves of knock intensity, which have been referred to as 'knock integrals', were determined by an inspection method which penalized fuels having the same maximum knock as the reference fuels, but which gave a knock persisting over a wider speed range, the same method appreciating fuels which gave the same maximum knock as the reference fuels, but over a narrower or lower speed range. In effect these results are comparable with those which would have been obtained had the areas under the knock curves been measured with the speed base modified to a time base. This is probably the most accurate indication of the viewpoint of the user, although any results need to be qualified if slow-speed traffic driving and high-speed cross-country driving are considered separately.

(*h*) The ratings given as level road ratings are taken from the Uniontown results without alteration and are based on maximum knock intensity only. They refer only to 'unbranded' fuels.

(*j*) The Motor Method laboratory ratings are the final averages from nineteen laboratories as determined immediately before and also immediately after the road tests. The Research Method ratings are from determinations made by seven laboratories, and the ratings at 105° F. mixture temperature from determinations by one laboratory only, using a special mixture heater designed to reduce the change-over lag which occurs when the standard heater is used at low air temperatures.

TABLE II

Uniontown Test Results (expressed to the nearest octane no.)

Fuel no.	*Max. knock*	*Hill ratings*			*Laboratory ratings*		
		Extinction speed ratings	*Knock integral ratings*	*Level road max. knock*	*Motor method*	*Research method*	*105° F. mixture*
1	69	69	68	..	68	71	69
3	77	76	75	..	76	80	77
4	60	62	59	..	60	59	60
6	68	69	68	..	70	71	71
13	68	68	67	..	69	71	69
14	49	..	..	..	51	51	51
16	70	70	68	..	70	72	71
12	72	68	73	73	71	80	76
5	67	66	65	67	66	70	69
10	67	65	66	66	66	70	69
8	65	64	63	64	64	68	66
2	73	70	72	72	71	75	74
9	69	69	68	69	69	72	71
11	75	74	75	75	74	79	76
7	71	68	72	71	68	73	70
15	73	72	73	73	72	73	72

It is obvious from Table II that Research Method ratings do not give a satisfactory indication of road behaviour for present-day cars, and the ratings with the mixture temperature adjusted to 105° F. also tend to be high in many cases. If the mean deviations from complete correlation with the Motor Method are averaged for the maximum knock, extinction speed, and knock integral ratings, it is found that the laboratory ratings by the Motor Method are 0·6 numbers low, 0·3 numbers high, and 0·1 numbers high respectively, to the first place of decimals. The mean deviation averaged from all three methods of analysing ratings, giving each equal weight, is about 0·13 numbers, the Motor Method giving a low average by this amount. This is, of course, entirely negligible when the necessarily approximate nature of road tests is taken into consideration.

Further evidence to show the certainty that no major change to the Motor Method is required may be obtained by deliberate prepossession in favour of any selected fuel by assuming that the car or cars which rate this fuel the highest (or, if desired, the lowest) were not used in sufficient numbers to be representative of the distribution of such cars on the road. For example, it might be assumed that there were insufficient cars used of the type which rated the benzole blend high (fuel No. 7, see below). If the ratings are determined only from the results from the six cars of different makes which rated this blend the highest, it is found that for no fuel does the final average differ from the official rating by more than one octane number. This is obviously an extreme and unfair example, but affords ample proof that the laboratory method is as typical of road results as can be expected.

With regard to the fuels used, the first eight in the table of test results were obtained from manufacturers' depots and were representative of motor fuels sold throughout the U.S.A. They differed negligibly in distillation range and vapour pressure, chemical type, &c., from fuels sold during the same period in Great Britain, but did not include a benzole blend or an alcohol blend. The remaining fuels were obtained specially for the tests to represent fuel types of interest to the oil industry and were as follows:

Fuel no.	*Type.*
12	Cracked gasoline.
5	Cracked gasoline.
10	Fuel 12 blended with a low octane number straight run.
8	Fuel 5 ,, ,, ,, ,,
2	Fuel 10 plus tetra-ethyl lead.
9	Fuel 8 ,, ,, ,,
11	Fuel 5 ,, ,, ,,
7	Straight run low octane plus benzole.
15	California straight run gasoline.

Study of the test results shows that the only fuel not well rated (when all methods of interpreting results are considered) by the Motor Method is the benzole blend, the laboratory rating being low. Tests made in Great Britain show the same order of discrepancy for alcohol and alcohol/benzole blends. The cause of the disagreement is not completely understood, but a recent suggestion is that it depends on the effect of volatility and the distribution of anti-knock material in the fuel in conjunction with events in the engine manifold during acceleration.

While work is proceeding to improve this item of correlation it has been considered desirable by the Standardization Committee of the Institution of Petroleum Technologists to permit an adjustment to be made to octane numbers of benzole and alcohol blends which will give ratings in closer agreement with road averages. This adjustment depends on determination by chemical means of the aromatic content of the fuels tested, suitable precautions being taken to eliminate the risk of the method introducing a correction for cracked gasolines, and making a correction on the basis of this chemical test. A similar correction is also permitted in the case of alcohol blends. Details of the method are given in the 1935 edition of the Standard Methods of Test of the I.P.T.

Such methods of adjusting ratings are, clearly, only tentative, and it is to be hoped that countries which are particularly interested in these special fuels, and which may feel the need for further investigation into methods for rating them, will bear in mind the importance of maintaining an international standard engine and method of laboratory test, and endeavour to secure accuracy of correlation by attention to instrumentation on the laboratory engine rather than by adopting a different technique for the engine itself which will, inevitably, destroy the accuracy of ratings for other fuel types much more typical of world distribution.

Engine Severity Factors

Since the 1935 Uniontown tests a new method of rating car engine performance has been developed. This is known as the 'Engine Severity Factor' and is a value which is supposed to indicate how much a given car engine differs from the C.F.R. Motor Method in rating fuels, and how far the design is good from the knock point of view (Veal [2, 1935]).

The severity factor is defined as:

$$\text{severity factor} = \frac{\text{research method rating} - \text{road rating}}{\text{research method rating} - \text{motor method rating.}}$$

If a car rates fuels the same as the Motor Method the severity factor becomes 1·0. One rating equally with the Research Method has a factor of 0·0, and a car rating midway between the two laboratory methods has a factor of 0·5, &c.

This factor is suggested as being an indication of the amount by which a given car engine is open to improvement, the lower the factor the better the engine.

There is scope for the introduction of some such value for grading car engines, but the proposed formula is only valid if the C.F.R. ratings of fuels tend to alter in linear, or at least in unidirectional, relation with change of mixture temperature. Actually this is not the case. One fuel may show a steady increase in octane number from, say, 68 to 73 between the Motor Method and the Research Method conditions, while a second may have a Motor Method octane number of 68, an octane number of 75 at a mixture temperature of 150° F., and an octane number of only 72 by the Research Method.

It was observed at the beginning of the section dealing with the Uniontown tests and the Motor Method that tests with an unheated mixture and 600 r.p.m. in the laboratory engine are not typical of any normal car engine, and thus any factor based on Research Method values may be entirely misleading.

If a fuel has C.F.R. ratings which first rise and later fall as the mixture temperature is reduced, the proposed factor would become zero for either a car engine equivalent to a relatively high C.F.R. temperature or for one equivalent to the Research conditions (if this were possible). It would be negative for an engine equivalent to the C.F.R. at some temperature higher than the Research Method, with values rising to zero for car engines which were both slightly better and slightly worse than this.

The difficulty might be overcome and a factor developed which would be of practical value in connexion with grading car engines if C.F.R. temperatures of 300° F. and, say, 100° or 150° F. were chosen for the two conditions of laboratory test, both tests being made at 900 r.p.m.

Knock Ratings of Aviation Fuels

At the time of writing (April 1935) the methods to be used for rating aviation gasolines are under re-examination. In the U.S.A. the Motor Method values are accepted, provided the aromatic content or cracked gasoline content of the fuel does not exceed a certain limit determined by a chemical test (the 'acid heat' test), but no allowance is made for the fact that, even though it may be correct to de-grade such fuels for certain aero engines, the addition of further aromatics, &c., might, if the freezing-point specification were still met, give satisfactory fuels.

In Great Britain the C.F.R. test with a mixture temperature of 260° F. is used, other conditions being the same as for the Motor Method.

Further research is proceeding in both countries to explore the effect on correlation with service type engines of the most recent types. As the information at present available does not seem consistent with the adoption of an international method for testing aviation gasolines, and as later results may modify any conclusion which can be reached, it is not intended to enlarge on this aspect of knock testing in this article.

REFERENCES

1. VEAL, C. B. *Proc. 15th Annual Meeting, Amer. Petr. Inst.* **15,** Sec. III, 33 (1934).
2. —— *J.S.A.E.* **36,** 165 (1935).

ENGINE ASPECTS

17. THE ENGINEERING ASPECTS OF DETONATION

By C. O. B. BEALE
Ricardo & Co. (1927) Ltd.

THE engineering aspects of detonation can conveniently be regarded from three main viewpoints: firstly, from the point of view of the designer; secondly, of the operator who is interested in the engine's performance and in the troubles caused by detonation; and thirdly, of the testing and research staff in their work on the test-bench. All these three subdivisions are, of course, more or less interconnected, but it will probably be easier to follow the arguments if an attempt is made to divide the subject in this way.

Design

In every engine design, after steps have been taken to ensure quietness and smoothness of running, the principal aim is directed towards high power output and low fuel consumption. In unsupercharged engines, which form the vast majority produced to-day, in order to obtain the highest power output it is first necessary to aim at the highest possible volumetric efficiency and then to use as high a compression ratio as possible without detonation. In striving after a low fuel consumption the volumetric efficiency has but little influence, and it is the compression ratio which is the determining factor. In the case of supercharged engines the conditions are rather different, since the changes have to be rung between the degree of supercharge and the compression ratio, but this special case will be considered later.

It has been said that the highest compression ratio must be used consistent with freedom from detonation. This needs some qualification, and, in order to determine what this qualification is, it is useful to examine the effects of raising the compression ratio, assuming that a fuel is used which will not detonate in any circumstances.

As the compression ratio is raised the power output rises, but the rate of increase falls and becomes small at high compression ratios. There is a gain of 8% between a compression ratio of 5 : 1 and 6 : 1; 6% between 6 : 1 and 7 : 1; and only 4% between 7 : 1 and 8 : 1. The gain in efficiency behaves in the same way and tails off from 9% between 5 : 1 and 6 : 1 to about 5% between 7 : 1 and 8 : 1. The effect on exhaust valves of raising the compression ratio is unconditionally good since the exhaust temperature falls as the compression, and therefore expansion, ratio is increased. The reverse is the case with sparking-plugs, and a better and better heat-resisting plug is necessary to avoid pre-ignition as the compression ratio is raised. Apart from being more expensive, plugs which are good in heat-resisting qualities suffer from the disadvantage that they will not so readily fire a weak mixture and that they are very prone to oil up. The most disadvantageous of all effects of raising the compression ratio is the rapid increase in maximum cylinder pressure. At a compression ratio of 5 : 1 the maximum cylinder pressure is about 500 lb. per sq. in., at 6 : 1 it is about 650, at 7 : 1 it has risen to about 800, and at 8 : 1 it is about 950 lb. per sq. in.

With the foregoing effects in mind, it is possible to decide what compression ratio would be chosen, always assuming that the fuel would not detonate. Since the gain in power and efficiency at a compression ratio higher than 8 : 1 is small, and since the maximum pressures have risen to so high a figure, it can be said that it is hardly ever worth while to use a higher compression ratio than this.

In the case of small engines up to about 2½-in. bore, the minimum scantlings permitted by foundry and production considerations will nearly always mean that the strength and stiffness of the parts will be adequate for this compression ratio of 8 : 1. For large engines of 5-in. to 6-in. bore this does not apply, and in order to avoid using parts either heavier or made in expensive material, the compression ratio would be fixed at about 6 : 1.

Having decided what compression ratio would be used in unsupercharged engines with a non-detonating fuel, the question arises as to how nearly this ideal can be approached with the fuels available for transport and industrial purposes, and what steps can be taken in the engine design to reduce detonation.

Some 10 years ago attention was only just beginning to be paid to the anti-knock properties of fuels, and at that time detonation intervened long before this ideal compression ratio was reached. For small engines the highest compression which could be used was in the neighbourhood of 5·5 : 1 and for large engines not much more than 4·5 : 1. Since then there has been a considerable improvement in fuels, and the corresponding figures are rather over 6·0 : 1 for small engines and about 5·0 : 1 for large engines. These figures are based on the assumption that the engine design is the same, and the greater increase in the permissible compression ratio for small engines is due to the fact that the 'No. 1' fuels have been improved to a greater extent than the commercial fuels. It is generally found that 'No. 1' fuels are used for small engines, since these are mostly fitted in private cars: often enough there is a good reason for using 'No. 1' fuels in private cars, since these are often used for short journeys, and a fuel with good volatility is desirable to allow the engine to run satisfactorily without warming up.

When a design is being prepared, it is known nowadays within close limits what fuels will be available and therefore how much help can be expected in that way. Over and above this, the anti-knock qualities of the engine will depend mainly upon the design of the combustion chamber.

A great deal of research has been carried out, first to discover the factors influencing detonation, and secondly to apply this knowledge to improving engine design from this point of view. It was thought at one time that turbulence of the gases had a large influence upon detonation, but it appears now that this is not so, provided that the turbulence is of the same intensity throughout the combustion chamber. It seems to be established that it is the length of flame travel from the sparking-plug to the most distant part of the combustion chamber which is the deciding factor in controlling detonation.

Once this is realized, it is easy to see why some engines detonate very much more readily than others. The worst possible case is probably that of the side-valve T-headed engine, with the inlet and exhaust valves in side pockets on opposite sides of the cylinder, and with the sparking-plug over the inlet valve, and probably the best case is exemplified by the Ricardo Turbulent head in which side valves are used and in which the combustion chamber is limited to the space over the valves and over a part of the cylinder bore. The space over the remaining part of the piston area is rendered inoperative as far as detonation is concerned by allowing only gasket clearance (about $\frac{1}{16}$ in.) between the piston crown and the head at top dead centre. The sparking-plug is placed nearly in the centre of the top face of the combustion chamber—actually with a slight bias towards the exhaust valve—and in this way the length of flame travel is reduced enormously.

If it is desired to use overhead valves, the best arrangement is with a pent-roof head with inclined valves and with the sparking-plug at the apex. This is good, but is also expensive since it involves the use of two camshafts. The more usual method is to have a single row of valves disposed vertically. If the combustion chamber is made to cover the whole of the bore, the length of flame travel from the plug at one side must be at least equal to the bore and is therefore nearly twice that of the pent-roof type head and of the Ricardo Turbulent head. The distance can be much reduced by using dual ignition with another plug fitted on the other side of the head, but this again is expensive and it is necessary to ensure synchronism between the two plugs. The overhead-valve engine with a single row of valves can be dealt with in the same way as the side-valve engine by offsetting the combustion chamber complete with the valves to one side of the cylinder bore, and again rendering the rest of the cylinder bore inoperative by a small piston to head clearance.

These, then, are the ways of securing a compact combustion chamber for side-by-side and overhead-valve engines, thereby enabling a higher compression ratio to be used than would otherwise be possible without detonation. It is found in practice that, by adopting one or other of these principles, it is possible to raise the compression ratio by rather over 0·5 ratio.

Although the compactness of the combustion chamber has the greatest influence upon the compression ratio which can be used, there is a considerable advantage to be gained in practice by the use of an automatic advance and retard mechanism to control the ignition setting for engines which have to work over a wide speed range such as in vehicles. Work on the test-bench will show the speed at which the tendency to detonate is greatest, and the highest compression ratio which can be used at that speed when the ignition timing is correctly set for that speed. If the compression ratio is fixed so that detonation just does not take place at this point, which will usually be found to be about half-way up the speed range, any reduction in speed will immediately necessitate resetting the ignition point and will mean, in a vehicle, continuous adjustment of the ignition lever. This would be intolerable, and to avoid this it will be necessary to lower the compression ratio so as to permit of the ignition being considerably over-advanced beyond the correct setting at low speeds before detonation sets in.

This can all be avoided by the fitting of a speed-controlled automatic timing mechanism, which gives the ignition timing found correct over the speed range. It is found that a compression ratio at least 0·25 ratio higher can be used if an automatic advance is fitted than is practicable with manual control only.

A further most desirable accessory is the combined speed and load-controlled automatic ignition timing. At light loads the correct ignition setting is considerably more advanced than at full load. This can be achieved with a manual control only or with a combined manual and automatic speed control, but it necessitates setting the full advanced position earlier than is required for full load, and leaves the driver to retard the ignition as the throttle is opened in order to obtain the best power output and to avoid detonation. If the contact breaker mechanism is suitably connected to the inlet pipe, then the variation in depression in the inlet pipe can be made to alter the timing and again to follow the correct curve over the load range.

When everything possible has been done in the engine design and with the use of present-day fuels, it is found that small engines can use a compression ratio of about 7 : 1 and large engines about 5·5 : 1 on fuels of 65–70 octane number.

The actual figure to be used in each case must be settled by test-bench and road work, and the methods of doing this will be discussed later.

It is often imagined that the use of a high compression ratio necessarily is accompanied by rough running. This is not so, but it is liable to occur unless it is understood what causes roughness. The fact of the maximum pressure being high does not mean in itself that the running will be rough, neither is it only the rate of rise of pressure in the cylinder which is the controlling factor, but it is rather the rate of change of pressure rise from the compression to the firing line on an indicator diagram which causes roughness. The last two effects tend to go hand in hand unless precautions are taken. In a side-valve engine with a turbulent head, the rate of pressure rise can be controlled by the area of the communicating passage between the cylinder and combustion chamber, and can be kept to a figure of about 30 lb. per sq. in. per degree of crankshaft rotation, and at this figure the performance will be good and roughness avoided. In overhead-valve engines the general difficulty at low compression ratios is to obtain a high enough rate of pressure rise, and it is fortunate that this rises of its own accord as the compression ratio is increased, and is found to be at about the right figure at the compression ratios which it is desired nowadays to use.

So far, then, the case of unsupercharged engines for vehicle and industrial use has been considered, and it has been shown that, even with the best modern design and present-day fuels, it is detonation that limits the compression ratio that can be used, and that the power and efficiency is reduced by at least 5% below that which could be obtained without the employment of special materials or stronger components.

In the case of supercharged engines it is not possible to evaluate simply the loss in performance which must be accepted owing to detonation. Whereas, in unsupercharged engines, the compression ratio is fixed after the best possible breathing has been obtained, the reverse is the case when a supercharger is fitted. The compression ratio is settled first of all in the interests of fuel economy and heat flow, and as much supercharge is applied as is allowed by the anti-knock quality of the fuel.

A concrete case will illustrate and evaluate the interrelation of supercharge and compression ratio. A fuel is chosen which will allow an engine to be run unsupercharged at a compression ratio of 6·1 : 1 with a certain intensity of detonation. The fuel is changed for another with a higher anti-knock value which will allow the compression ratio of this engine to be raised to 7 : 1 with the same intensity of detonation. The gain in power in this case is 6%. If the compression ratio is left at the original figure of 6·1 : 1, and advantage is taken of the better fuel to supercharge the cylinder, it is found that, on the same engine, the intake pressure can be raised to 4 lb. per sq. in. above atmospheric before the same intensity of detonation is reached. This gives an increase in power of 36%, without taking into account the power absorbed to drive the blower.

This example makes it very clear that an increase in intake pressure is far more effective than raising the compression ratio in its effect on power output if a better fuel is available, and similarly, for a given fuel, a high supercharge and a low compression ratio will give the highest power.

It is also found that the maximum cylinder pressures increase much less rapidly in proportion to the gain in power if a high supercharge is used rather than a high compression ratio. On the same engine referred to above, when use was made of the better fuel to raise the compression ratio while keeping the intake at atmospheric pressure, the maximum pressure rose from 660 lb. per sq. in. at a compression ratio of 6·1 : 1 to 780 lb. per sq. in. at 7 : 1 for an increase in power of 6%. When the compression ratio was unaltered and the intake pressure increased, the maximum pressure rose from 660 to 920 lb. per sq. in. for an increase in power of 36%.

It is therefore clear that a high supercharge and a low compression ratio are beneficial as regards power output and maximum cylinder pressures, also as regards sparking-plugs which will not have to be of such a high heat-resisting quality as if a high compression ratio and low supercharge were used. But this leaves two factors of major importance which will be adversely affected—fuel consumption and exhaust valves. If use is made of a better fuel to increase the intake pressure while leaving the compression ratio unaltered, the specific fuel consumption remains practically unchanged. It will decrease slightly due to greater mechanical efficiency if no account is taken of the power absorbed by the blower, and may again be slightly better due to improvement in distribution in a multi-cylinder engine, but these sources of improvement will almost certainly be more than offset by the blower loss.

The heat flow, and therefore distress, to the exhaust valves will increase as the intake pressure is raised, and the combination of a high supercharge and low compression ratio will render frequent overhauls necessary or may so shorten their life that the engine becomes of academic interest only.

There are thus two conflicting factors, and the compression ratio must depend upon the use to which the engine is to be put. If a short life does not matter, and fuel consumption and reliability are of no consequence, it can be low; if, on the other hand, reliability is vital and economy and long periods between overhauls is of first importance, then it must be high and the supercharge and therefore power output curtailed accordingly.

In aircraft engines the compression ratio generally chosen is between 6 : 1 and 7 : 1. A few years ago detonation set the limit to the amount of supercharge that could be applied, but lately the anti-knock values of aircraft fuels has increased to such an extent that in some cases the limit is now set by heat flow to parts such as pistons.

Detonation as affecting the Operator

Dealing firstly with transport and industrial engines, it can be said that detonation is only objectionable in that it offends the ear in its early stages, and in that it will turn into pre-ignition if it is allowed to persist with any but moderate intensity. In such engines, which are of comparatively low duty, detonation will not cause damage to the engine parts.

It is very noticeable that the noise caused by detonation varies with different types of engines. In engines with overhead valves the noise generally takes the form of a high-pitched tinkling knock, whereas in side-valve engines it is deeper and lacks any musical note. The explanation is probably to be found in the relative stiffness of the two structures which will produce a different sound when struck by the detonation wave. It is also very noticeable that when detonation takes place in a turbulent head the noise is more violent than in the conventional side-valve head. It is suggested that, owing to the compact form of the turbulent head, a comparatively large amount of gas detonates as compared with thin layers lying about in odd corners in a conventional type head.

The addition of benzole to petrol is well known to improve the anti-knock value of the fuel, and on road vehicles it is often credited with more than its true worth. On an ordinary petrol, detonation will start almost immediately the throttle is opened wide if the conditions are suitable, whereas on a benzole mixture, which will give the same intensity of detonation under steady running conditions, there is a considerable delay in the building-up of detonation to its steady intensity. The time taken to reach the maximum value may be anything up to 10 seconds or more, and in this time the hill may have been surmounted or the obstruction passed and the driver will not have heard any detonation. This delaying action of benzole is not noticed when testing fuels in the laboratory for anti-knock value, since all conditions are allowed to become stable before readings are taken.

The use of lead tetraethyl is now very common to raise the detonation point of fuels. At one time there was strong evidence that it had a detrimental effect upon the engine parts, particularly the exhaust valves, but it appears that damage was only caused when the design was faulty. At the present day there is no need to fear harm to the engine from the small quantities of lead tetraethyl used in fuels ordinarily available.

In high-duty engines such as are used in aircraft, detonation is a very serious matter, and may completely wreck the engine if allowed to persist for more than a very short time. The intensity which can be tolerated or the time for which it may be allowed to persist varies with different engines and has to be determined experimentally. The observed effect on pistons and cylinder heads is a pock-marking of the surfaces in the initial stages, and, when more severe, the surfaces are burnt or eroded and, in the case of a piston, will cause seizure.

Detonation on the Test-bench

In considering detonation in relation to design, it was shown that an approximate estimate could be made of the compression ratio which could be used. The precise figure must be determined on the test-bench and subsequently confirmed in actual service, particularly in the case of vehicle engines where the air temperature under the bonnet and the degree of carbonization cannot exactly be foretold.

First of all the speed must be found at which the tendency to detonate is the greatest, and this will be generally at a speed slightly below that at which maximum torque is developed. The optimum ignition advance must then be found by taking a series of torque/ignition curves at speeds around that at which maximum detonation is expected. These torque/ignition curves show the rise or fall of engine torque with various settings of ignition timing, and are taken on full throttle, at constant engine speed, and with a fuel which will not detonate even when the timing is advanced considerably beyond the setting giving maximum torque. The timing should be advanced and retarded beyond the optimum by about 15 to 20°, so that there is a definite fall in torque from the maximum. The timing giving maximum torque can thus be very accurately found for each speed, and the optimum ignition advance curve drawn covering the speed range in question.

A fuel is then chosen which will detonate if the ignition is advanced beyond the optimum setting, and a curve of ignition timing, at which detonation reaches a certain intensity, is also plotted and compared with the optimum timing curve. It is clear that, where these two curves approach most closely, there is the least latitude for over-advance and that therefore at that speed there is the greatest tendency to detonate.

The engine is then run on the fuel which will be used in service, and another torque/ignition curve taken at the worst speed and the ignition setting advanced until detonation sets in. If the compression ratio is too high, it will be impossible to reach the optimum timing, and the power output will never reach the maximum. If too low detonation will not set in until the ignition has been advanced considerably beyond the position giving maximum torque on the non-detonating fuel used in the first instance.

If the turbulence is adequate, it is found that there is a range of about 5° on either side of the optimum ignition setting over which the torque is at a maximum. It is clear, then, that the highest compression ratio which can usefully be used is one which will just avoid detonation with an ignition retarded just far enough still to maintain maximum torque.

The advantage of an automatic ignition control mechanism, which will both accurately follow the optimum advance curve over the speed range and advance the timing at light loads, has been discussed, and if this is adjusted to give a timing just sufficiently retarded still to maintain maximum torque, the compression ratio discussed above could be used without the necessity for any adjustment by the driver while the engine was clean. To allow for carbonization, the compression ratio must be lowered, and it should be lowered by an amount which will just avoid detonation when the thickness of the carbon layer has built up to its maximum amount. This amount can only be determined experimentally.

When speaking of the performance of an engine either as regards its maximum torque which is usually expressed in lb. per sq. in. brake mean effective pressure or its maximum power in B.H.P. per litre, it is only too often that no mention of the fuel is made. A certain performance, even if the compression ratio is specified, means very little if the fuel is not known, since it is the anti-knock quality of the fuel which limits the performance. If an engine is reported to give a torque of, say, 125 lb. per sq. in. B.M.E.P. without specifying the fuel, very little information is conveyed as to whether the design is good, bad, or indifferent, but if it will give this output on a commercial grade fuel it is good indeed. It follows from this that a comparison of the excellence of any two engines is fully covered if the power, fuel consumption, and quality of fuel are stated. It is not even necessary to specify the cylinder size, since it is found that the gain in efficiency, due to the higher compression ratio possible with smaller cylinders, is just offset by the higher heat loss. It has been found that the fuel consumption at the most economical mixture strength on present-day commercial fuels of a large number of engines of equally good design with cylinder sizes varying from 250 c.c. to 1,500 c.c. is 0·45 pts. per indicated h.p. per hour (=0·26 litre per 1 h.p. per hour).

Even nowadays pre-ignition is often confused with detonation. Pre-ignition is the igniting of the charge by some hot point other than the spark, and is generally done by an overheated sparking-plug electrode or an exhaust-valve head. It may be mentioned in passing that it is a popular belief that ragged pieces of metal in the combustion chamber, such as the end of the sparking-plug threads, will become incandescent and cause pre-ignition, but it is found in practice that this is very seldom, if ever, the case.

Pre-ignition is really a special case of the general principle, the charge being ignited by some agent other than the spark. The temperature of the exhaust valve on full load is nearly always above the self-ignition temperature of the charge, but ordinarily the time element prevents self-ignition taking place before the spark has passed. Nearly every engine will continue running for a period spasmodically at idling speed if the ignition is switched off when the engine is running on full load, and this is so simply because there is a comparatively long time for the charge to be in contact with the hot surface of the valve or sparking-plug.

The combination of temperature and engine speed may be sufficient to fire the charge at the running speed later than the normal time of ignition by the spark, and in these circumstances the engine will continue running with the ignition switched off but at a reduced power output. An appropriate increase of temperature will cause self-ignition to take place at the same time as the spark passes, and, in this case, the engine will continue running at the same speed and developing the same power whether the ignition is working or not. A further increase in temperature will cause this self-ignition to occur before the spark has passed, and it is this which is pre-ignition and which is therefore a totally different process to detonation.

The two are, however, to some extent interconnected, in that persistent heavy detonation may so heat up the sparking-plug or exhaust valve that pre-ignition will result. Again, pre-ignition may cause detonation in exactly the same way as too early an ignition timing; in fact, it is probably this sequence of events which has led to the confusion between the two separate phenomena. Pre-ignition is always silent, indeed it must be so from a consideration of its cause, but it may be accompanied by a heavy knock, which is a detonation knock caused by the too early ignition, and it is often this heavy detonation knock, occurring suddenly without preliminary slight detonation, which indicates that pre-ignition is taking place.

It is difficult to define the intensity of detonation which can be allowed before the power is affected, because no satisfactory method of evaluating the intensity of detonation has been devised which is applicable to all engines (see Art. 15). In a variable compression engine, that is to say, an engine on which the compression ratio can be varied while the engine is running, the tolerable intensity of detonation can readily be found by the point at which the increase in power, by raising the compression ratio, on a fuel which is detonating starts to diverge from that realized on a non-detonating fuel. On an engine of fixed compression ratio this can only be determined by using various fuel blends which give different degrees of detonation, and by comparing the power in each case with that obtained on a fuel which does not detonate. It can be said generally that slight detonation will not lower the power output, and that it has to reach a moderately heavy intensity, such as is extremely obvious to the ear, before this happens.

The same thing applies to the cooling water temperature. Slight detonation will not increase the heat loss to tne cooling water, and it is found that the intensity has to become great enough seriously to lower the power output before a measurable effect upon temperature of the cooling water is recorded.

It may be well to summarize briefly the conclusions reached.

Summary

Design.

1. Principal aim is high power output and low fuel consumption. Power is controlled by volumetric efficiency and the compression ratio, fuel consumption by compression ratio alone.

2. Assuming that the fuel will not detonate, the compression ratio which would be chosen for unsupercharged engines is about 8 : 1 for small engines and 6 : 1 for large engines.

3. With the fuels commercially available, detonation prevents these compression ratios being used for transport and industrial purposes. With present-day fuels, compression ratios of rather over 6 : 1 can be used for small engines and about 5 : 1 for large engines if the cylinder head design is conventional and if manual control only is provided for the ignition timing.

4. Combustion chamber shape greatly affects detonation. Length of flame travel is the important consideration. This can be shortened in side-valve engines by offsetting the combustion chamber as in the Ricardo Turbulent head, and an improvement made in overhead-valve engines in a similar way. A compact combustion chamber achieved in this way will allow the compression ratio to be raised by about 0·5 ratio as compared with a conventional type of head.

5. If the ignition advance is automatically controlled both by speed and load, a further increase in compression ratio of about 0·25 ratio can be used.

6. If these two factors are incorporated in the design, small engines can now use a compression ratio of about 7 : 1 and large engines about 5·5 : 1 on fuels of 65–70 octane number.

7. Roughness of running does not necessarily accompany the use of a high compression ratio, but may do so unless the causes of roughness are understood and precautions taken. High maximum pressures do not cause roughness, but it is the rate of application of pressure which matters.

8. For supercharged engines and with a given fuel, a greater power output is realized with a low compression ratio and high supercharge, but fuel consumption and reliability suffer. For aircraft engines a compression ratio of 6 : 1 to 7 : 1 is chosen, in the interest of economy and heat flow, and a moderate supercharge used.

9. An experiment is recorded showing the comparative effects of making use of a certain fuel of higher anti-knock value, firstly by raising the compression ratio with no supercharge, and secondly by applying supercharge with the compression ratio left unchanged. For equal intensity of detonation the gain in power by supercharging was 36%, and by raising the compression ratio was 6%.

Operation.

10. In transport and industrial engines, detonation is objectionable only because of the noise and because it may lead to pre-ignition.

11. Noise caused by detonation varies with different types of head.

12. Benzole added to fuel causes a delay in the building-up of detonation to the steady intensity. Lead ethyl nowadays causes no damage to engine parts in the small concentrations commercially used.

13. Detonation in high-duty engines, such as for aircraft, is very serious and may wreck the engine in a few minutes by causing seizure.

Test-bench.

14. Correct compression ratio is determined by torque/ignition curves. Correct ignition advance is first found over speed range with non-detonating fuel, then the speed is determined at which detonation is greatest, next the compression ratio is adjusted so that correct ignition advance can just be used at that speed with no detonation with the fuel to be used in practice.

15. Comparative performance of any two engines is fully covered if power output, fuel consumption, and quality of fuel are stated. Statements of performance mean very little if fuel is not specified. Fuel consumption remains unaltered with different cylinder sizes if the compression ratio is adjusted to give the same intensity of detonation.

16. Pre-ignition is totally different from detonation, but the two are interconnected. Pre-ignition caused by the charge being ignited by some hot point before the spark passes. Detonation may cause pre-ignition by heating up the sparking-plug electrodes or the exhaust valve. Pre-ignition is always silent, but may cause a detonation knock from the same cause as a too early ignition timing.

17. No satisfactory method of evaluating detonation applicable to all engines has been devised. In a variable compression engine, the permissible intensity before the power is affected can be determined by comparing the increase in power by raising the compression ratio on a fuel which detonates and one which will not. On fixed compression engines the only way is to use fuel blends giving various degrees of detonation, and to compare the power output of each blend with that given by a non-detonating fuel. Generally speaking, a moderately heavy intensity is necessary to affect the power.

18. Effect of detonation on heat loss to the cooling water is negligible until detonation becomes heavy.

PART V

BITUMINOUS MATERIALS AND THEIR PRODUCTS

SECTIONS 43 AND 44

SECTION 43

OIL SHALES, TORBANITES, CANNELS, ETC.

OIL SHALES, CANNEL COALS, AND TORBANITES

By MARTIN J. GAVIN, B.S., E.M.

Chief Engineer, Oil Division, Consolidated Steel Corporation, Limited, California

Oil shale and its richer varieties—cannel coals and torbanites—are rocks which contain organic matter that on heating yields petroleum-like oils. They are widely distributed throughout the world and are generally regarded as important future sources of supply of hydrocarbon oils. For many years they have constituted the raw materials for small but locally important industries in Scotland, France, and Australia.

To produce oil from oil shale, the shale is mined, usually by methods similar to those used in mining coal, crushed or broken to a size suitable for further handling, and charged into a retort where heat is applied. At sufficiently high temperatures, in the absence of oxygen, the organic matter in the shale, commonly called kerogen, breaks down or decomposes—a process known as destructive distillation or pyrolysis—and changes into oil, gas, and fixed carbon. From the crude shale oil, products closely resembling those commonly produced from petroleum can be made by distillation and refining processes similar to those used in refining petroleum. The gas produced in retorting is combustible and its yield and heating value may be sufficient to furnish all the fuel needed for the retorting process. The fixed carbon usually remains in the shale residue—spent shale—although in some retorting processes the carbon is burned in the retort or converted into fuel gas by the same type of reaction used in making water gas from coal. The spent shale usually has no commercial value, although in some countries it is reported to be suitable in chemical composition to be used as a raw material in cement manufacture. Generally, however, spent shale is simply a residue which must be disposed of as waste material.

The production of shale oil is thus comparable in many respects with many of the low-grade ore-mining industries of the world, in that a large weight and volume of raw material must be mined to obtain a relatively small percentage of a concentrate for final refining into useful articles of commerce. Also, as in the low-grade ore industries, after the valuable material has been recovered as a concentrate, a large amount of waste remains to be disposed of. To produce shale oil in economically important quantities, the same general types of organization and operation are required as are used in these metal mining and refining operations; a highly efficient organization amply staffed with skilled scientists and technicians, and a large-tonnage handling of a raw material, each ton of which yields but a small amount in quantity or value of concentrate or finished commodity.

General Nature and Distribution of Oil Shales

Since cannel coals and torbanites usually occur in deposits that are small and economically unimportant except in a purely local sense, the outline below is confined mainly to those oil-yielding materials usually known as oil shales, deposits of which are widely distributed throughout the world and have been reported in the sedimentary strata of almost every country.

Generally, but not always, the better oil-yielding shales are brown or black in colour, break with a conchoidal fracture, and give a dark-brown streak. As a rule they are somewhat flexible or elastic, and the mineral matter is fine grained and usually free from grittiness. The richer shales usually resist weathering to a remarkable degree. Most oil shale is finely laminated, a property best noted in the spent shale, or on the surface of weathered exposures, but usually seen distinctly when sections of the raw shales are examined microscopically. In most deposits thin layers of rich and lean shale alternate; the layers of different richness probably represent alternating periods of rich vegetable growth followed by water overflow and sedimentation. The oil yield from different shales ranges from a trace to as much as 150 gallons per ton—the latter from some of the rich cannels and torbanites.

Much has been written concerning the occurrence and nature of oil-shale deposits in different parts of the world, although most attention has been paid to those deposits which yield oil in notable amounts. Little comment has been made on the much larger quantity of more widely distributed deposits of materials which are true oil shales but yield only small amounts of oil.

The following brief summary includes only those shale deposits which have been worked commercially for the production of oil or which have been studied extensively in anticipation of the time when they will be commercially utilized. For more complete presentations with extensive references, the reader is directed to the work of McKee and his associates [13, 1925] and to an earlier publication of the writer [9, 1924].

The Scottish oil shales have constituted the raw material for an important industry which began in 1850 and has continued to the present. The material first worked was a rich cannel coal or torbanite which yielded up to 130 gallons per ton, but this deposit was soon exhausted and leaner shales were then used. In recent years the average yield of oil was approximately 25 U.S. gal. per short ton. The Scottish deposits of importance are in a well-defined field, in West and Mid-Lothian, south of the Firth of Forth and mostly west of Edinburgh, the centre of the field being about 12 miles west of that city. These shales form part of the calciferous sandstone series at the base of the Carboniferous system, and yield an oil of good quality, low in sulphur, from which a complete range of petroleum-like products and excellent grades of paraffin wax have been commercially manufactured. The seams of oil shale, some 20 of which have been mined at different times, range in thickness from 3½ ft. to 8 or 10 ft. and are generally persistent but of varying thickness, and grade into lean or barren shale laterally. The seams are interstratified with ordinary carbonaceous shales ('blaes') which contain little or none of the characteristic organic material of the oil shales. The shale-oil industry of Scotland is fully described elsewhere in this work.

The more important oil-shale deposits of Canada are in New Brunswick and Nova Scotia, and these have been extensively studied by governmental and private agencies. In Albert County, New Brunswick, about 1860, a retorting plant was built and for several years shale oil was produced, refined, and used in New Brunswick and Nova Scotia. The competition of natural petroleum products terminated this work, and there has been no subsequent commercial shale oil production in this country.

The oil shales or torbanites of the Capertee and Wolgan Valleys of New South Wales, Australia, occur mostly in lenticular patches in the upper coal measures of Permo-Carboniferous age and were commercially worked from 1865 until recent years. Yields as high as 128 U.S. gal. of oil to the short ton have been reported, and much of the rich material was exported or used locally for gas-making. Here, again, a once-flourishing industry has been forced to suspend operations by the competition of low-cost imported petroleum.

The important oil-shale deposits of France are at Buxiere and Saint Hilaire (Allier) and at Autun (Saône-et-Loire). The first shale oil produced, of which there is definite record, was made from the Autun shales at least as early as 1839. The French shales yield from about 12 to 26 U.S. gal. of oil per short ton. The largest retorting plant is at Autun in the centre of a well-defined field having an area of some 250 sq. km. The shales are of Permo-Carboniferous age and in places contain large quantities of plant and fish remains. Because much of the organic matter in these shales can be removed by solvents and hence is not 'pyrobituminous', many writers do not regard these as true oil shales.

The oil shales of Esthonia, occurring in Palaeozoic deposits principally along the Gulf of Finland, in recent years have constituted the raw material for a rapidly growing industry. Pulverized shale has been used as a coal substitute as well as a source of oil. The industry in this country is covered in detail elsewhere in this work.

Within the past few years Japanese interests have been producing oil from the oil shales which overlie the coal deposits of Fushun in southern Manchuria. The oil yield is low, but since the shale must be removed in open-cut mining to reach the coal beneath, the cost of mining chargeable to shale oil production is small.

Before petroleum was discovered in Pennsylvania, numerous plants in the United States and Canada produced oil from shales, cannels, and bituminous coals. For several years the rich torbanitic Stellarite of Nova Scotia was exported to the east coast of the United States for gas-making and the production of oil. This early industry did not survive the discovery of inexpensively produced petroleum, and though many attempts have been made to establish commercial shale-oil production in different parts of the United States since 1915, none have succeeded. Enough experimental and large-scale development work has been done, however, to demonstrate that under favourable economic conditions the extensive oil-shale deposits of the country can supply very large quantities of oil as a substitute for petroleum.

The oil-shale deposits of the United States of probable greatest economic importance are those of the Green River formation of Eocene age which occurs in the States of Colorado, Utah, and Wyoming. These deposits contain thin seams which yield up to 90 U.S. gal. of oil to the short ton, while over an extensive area a total thickness of 35 to 40 ft. will yield an average of 35 gallons per ton. The shales vary greatly in richness within a relatively small vertical distance; in places a thin rich seam abruptly changes above and below into shale containing little organic matter. In other parts of the deposit there is a fairly gradual increase in richness over several feet, and then a similar gradual decrease to a lean or barren shale.

Other deposits of possible economic importance occur in Nevada and Montana, and there are extensive deposits of black shales in the eastern States—mainly Illinois, Missouri, Indiana, New York, Kentucky, Ohio, Pennsylvania, and Tennessee. The black shales occur mostly at one general horizon in the Upper Devonian—with some in the Lower Devonian and Ordovician—and usually in thick seams. In general, the oil yield is low, few samples yielding as much as 25 U.S. gal. per ton, while the average yield of the commercially workable seams is much lower.

The Origin of Oil Shales

The art of distilling bituminous or pyrobituminous shales to produce petroleum-like oils was known certainly as early as the last decade of the seventeenth century. In 1694 Eele, Hancock, and Portlock [8, 1694] distilled 'oyle from a kind of stone', and as early as 1681 a patent [2, 1681] was issued for the manufacture of pitch and tar from coal. The 'kind of stone' of Eele, Hancock, and Portlock was very possibly oil shale, but nothing of commercial importance came from these early efforts, the oils produced being used mostly for medicinal purposes. In passing, it may be mentioned that the early stages of exploitation of oil shales in most countries, even in recent times, have been marked by the 'discovery' of remarkable healing properties of shale oil. Since oils distilled from most shales have pungent, and, to most people, disagreeable odours, it is not difficult for the credulous to believe that they must have valuable medicinal properties.

The shale oil industry really began commercially in 1838 with the perfection of a refining process by Selligue [16, 1838], and the production of shale-oil products in France has continued from that time to the present. The better-known Scottish industry apparently originated independently of the French developments when James Young [19, 1850] regarded as the father of the Scottish industry, in 1850 patented his process for obtaining paraffin and oil containing paraffin from bituminous coals. When Young developed his process he intended to use a cannel coal, rather than what would now be called a bituminous coal, and in the Great Exposition of 1851 he exhibited products from the cannel coal of Boghead, near Bathgate, Linlithgowshire. This Boghead cannel was a small deposit, and by 1862 it had been practically worked out. Meanwhile, during a trial famous in British legal history [10, 1854–7], the court coined the term 'Torbane Mineral' for the Boghead cannel from its occurrence in the estate of Torbanehill, and this term soon became shortened to torbanite. The suit arose from a lease entered into between the proprietor of the estate and his mineral tenants which gave the lessees the right to work the coal on the property at a fixed royalty rate. As its value as a source of oil became generally known, the price commanded by the torbanite increased rapidly, and the lessor attempted to obtain a greater royalty for the mineral on the ground that it was not coal but a different material referred to as 'bituminous earth' and other indefinite names. The jury decided that, regardless of scientific evidence presented by some fifty witnesses, for the purposes of the lease the material must be regarded as coal. The decision was actually on a legal point and scientific evidence was virtually disregarded, although it was mostly to the effect that torbanite was not a coal.

From these beginnings the oil shale industry grew and flourished in Scotland, where it still exists although operating on a smaller and less profitable scale than in the early years of the twentieth century. Shale oil has been produced in commercial quantities in many countries, particularly in France and Australia, and more recently in Esthonia, but through the two centuries that have elapsed since Selligue patented his process, no sharp line of demarcation has been drawn between a coal and a shale, or between oil shales, cannel coals, and torbanites. Actually oil shales grade imperceptibly into 'barren shales' on the one hand, and into the torbanites or cannels on the other, and an origin common in general, though different in detail, may logically be attributed to all three.

Conacher [5, 1917] states that 'oil shales and torbanites form a group of materials which have in common the characteristic that on distillation they yield a product consisting of paraffin and olefins, and this feature is the source of their industrial importance'. According to Ashley [1, 1918], the line between a coal and a shale has never been sharply drawn, and he suggests that material that yields less than 33% of ash be considered a coal. Thiessen [18, 1921] writes that 'a shale is generally defined as a rock formed by the consolidation of clay, mud, or silt, having a finely stratified, laminated or fissile structure. When such a rock contains organic matter, it is termed carbonaceous or black shale, when the matter is of a bituminous nature it is called bituminous shale, and when rich in bituminous substances, yielding oil and gas on distillation, it is called oil shale.'

Many investigators, including the writer, have suggested that true oil shales are those from which only a small amount of the organic matter can be extracted by the usual solvents for petroleum. However, many of the shales commonly regarded as true oil shales yield organic matter fairly readily to such solvents as acetone and chloroform—some 50% of the organic matter of certain typical Colorado oil shales may be extracted from the shale by carbon tetrachloride or carbon bisulphide, although the extract is not an oil but rather closely resembles the so-called primary product of thermal decomposition of oil shale. Other investigators have privately informed the writer that with many shales solubility seems largely to be a surface phenomena—that solubility increases with decrease in particle size of the sample extracted. On the other hand, many oil shales are definitely almost insoluble in such solvents, apparently independent of particle size, and this is true of the typical oil-yielding shales of Scotland. It is probable that solubility of itself is not a means of classifying a material as a true oil shale, and in view of the extreme variation in the probable sources and original composition of the organic material in oil shales—in which term the writer includes bituminous shales, black carbonaceous shales, canneloid shales, cannel coals, torbanites, and kerosene shales—differences in solubility and other properties are reasonably to be expected.

Many investigators have offered evidence to explain various modes of origin of oil shales, and much of the evidence and many of the theories are conflicting. Unquestionably different conclusions have often been reached because different investigators worked with different shales, and much more study must be done before the various theories can be satisfactorily resolved. In general, however, there are two schools of thought, one holding that an oil shale is the remains of a petroleum deposit or oilfield, and the other that oil shales originated in the deposition of vegetable material with more or less silt or mud in quiet waters near shore lines and the subsequent alteration of the material due to decomposition and the lithification of the inorganic parts of the shale.

Microscopic examination of oil shales from all parts of the world shows that they are composed, in various proportions, of:

(1) Inorganic or mineral matter, such as argillaceous material, sand grains, pyrite crystals, and the like.
(2) A usually yellowish, brown, or dark opaque structureless 'groundmass' of organic material.
(3) Small carbonized or partly carbonized fragments of plants—often showing cellular structure—small spores, pollen, portions of the plant protective skin or bark.
(4) Yellow or reddish yellow, more or less spherical bodies considered by various investigators as algae, spores, spore cases, grains of resin, or globules of oil.
(5) Parts of the skeletons and scales of fish—sometimes a beautifully preserved complete skeleton—shells of small crustaceans, and the more resistant parts of insects.

It is generally held that the yellowish bodies and the dark groundmass are the sources of oil obtained by distillation, that these are probably of vegetable origin, or are petroleum as such or in some altered form, and that animal matter has not appreciably contributed to the oil-yielding material. The fact that little real oil can be extracted by the usual solvents for petroleum seems to preclude the belief that the yellowish spherical bodies are petroleum as such.

Microscopic study shows that the proportions of these constituents vary greatly with different shales. The organic part of the torbanite of Scotland consists almost entirely of the yellowish spherical bodies, while in many of the rich oil shales of the Green River formation in the United States the organic material is largely the formless opaque groundmass. All degrees of gradations exist between these two extremes with the typical oil shales of Scotland having an organic structure in which the yellow spherical bodies predominate.

Investigators in general agree that the mineral matter of most oil shales was deposited in fresh-water swamps or lagoons, but there are many theories as to the source of the oil-yielding material.

Bertrand and Renault [3, 1892] believe that the torbanites were composed of accumulations of microscopic gelatinous algae, which were preserved from complete decomposition by an antiseptic solution, possibly derived from their own decay, and that the antiseptic solution is now represented by the opaque organic matter of the shales.

Jeffery [11, 1914] disfavours the algal theory and suggests that the supposed algae are deeply sculptured coats of the spores of vascular cryptogams.

Steuart [17, 1912] concludes, from his own work and that of previous investigations, that 'oil shales may therefore be composed of (1) vegetable matter which has been made into a pulp by maceration in water and preserved by combining with salts in solution . . .; (2) rich materials of many kinds, such as spores, which nature has provided with means for protection against decay; and (3) a proportion of animal matter.' He also concludes that oil shale 'may be considered a torbanite containing a larger proportion of earthy matter from its original deposition or is simply a torbanite which has deteriorated with age'. He gives this reason for the variations in the organic matter:

'In accounting for the differences between different shales and between shale, torbanite, &c., we must remember that during the deposition of the sediments, as the lapse of time was very great, the climate must have varied to some extent, and the algae and plankton generally of the lagoon must have changed also, together with the shore vegetation producing pollen, spores, and seeds. The differences and varieties might have arisen from changes in the proportion of, or nature of, the humus, the spores, and the animal matter. And there are also the modifications produced by age, and the different conditions to which they have been subjected during their long history in the earth, such as warmth from depth or from proximity to intruded igneous rock.'

Scheithauer [15, 1913] believes that 'a large number of marine animals perished on certain occasions' possibly the result of volcanic eruptions, and states as evidence that the Scottish shale deposits have been shown to belong to the volcanic region.

Robertson [14, 1914] gives as his conclusions that 'there is little resinous matter in oil shales, and that the organic matter is a decomposition product of vegetable matter, of a nature like that found in peat and cannel coal, . . . and produced by a definite combination of external conditions'.

Davis [7, 1917] writes as follows regarding the microscopic studies he was making at the time of his death:

> 'It is clear that the structureless material of the Green River shales probably originated in a collection of plant debris which has, by decomposition and the activities of bacteria and other microscopic organisms, passed into a jellylike phase, which is to be found in certain kinds of peat deposits. The plant remains that have been found characterizing the shales from every locality from which they have been examined (Green River formation) are those of microscopic algae mixed in small percentage with pollen and similar parts of higher plants. Animal remains have been very rare in the material studied, and those noted were chiefly of insects in a very fragmental state.
>
> 'It seems apparent, therefore, that the study of the microscopic structure of these shales, as seen in vertical and horizontal sections, leads to the conclusion that the material was laid down originally in water, and that it passed through a series of stages of decomposition before consolidation and lithification had taken place. The remarkably well-preserved state of the delicate plant structures which have been examined indicates very slight disturbances of the original material and an almost entire lack of changes produced by the action of metamorphosing agencies since lithification.'

Cunningham-Craig [6, 1916] advances the theory that an oil-shale field may be considered as the relics of a former oil field. That is, oil formed in argillaceous deposits from vegetable debris has migrated into porous beds, and if any argillaceous beds of sufficient absorptive capacity exist in the vicinity of oil rocks, they will gradually absorb and adsorb the heavier and unsaturated hydrocarbons, and by their smaller porosity, especially if capped by impervious beds, will protect the adsorbed liquid from displacement by lixiviation, while inspissation is gradually modifying the petroleum in the direction of kerogen. Cunningham-Craig also believes that torbanite, &c., differ from oil shale in origin, and says that the former may be considered an incipient form of petroleum developed, adsorbed, and inspissated *in situ*.

The late David White (private communication 1926) believes that the groundmass is composed of products of the more or less complete biochemical decomposition of plant and animal matter, which is first held in colloidal solution in the water but later, under pressure of superimposed strata and incipient alteration, it becomes gradually solidified into a dense residue which surrounds and cements the detritus. The resinous or waxy outer coverings (exines) of spores and pollen grains of different kinds and from all orders of plants are also present. These are very resistant to decay in water, and occur in all shales and coals. Similarly resistant to decay and usually present in oil shales are portions of the skin or bark of plants that are cutinized through the secretion of horny, waxy, resinous or resin-oily matter. White subscribes to the theory that the yellow bodies are algae and states that these algae may be entirely absent, or scattered among the spore exines and cuticles of canneloid layers of coal or in cannels, or they may have been present and preserved in such great numbers as to constitute the greater part of the organic matter. He states that the bogheads, richest of all the oil-shale series, are made up almost entirely of such algae. Also sometimes present in considerable quantity are fragments of resin of different kinds, which were concentrated in the deposits by the decay of resinous wood. Occasionally small fragments of the more resistant woody tissue of plant or tree are present as shreds or ragged pieces impregnated by the groundmass or as fragments of so-called 'mineral charcoal' or 'mother of coal' (fusain).

Thiessen [18, 1921], after a preliminary study of a Scottish shale and of Devonian shales of Illinois, Indiana, and Kentucky, concluded: '. . . that the oil shales, as far as examined, do not contain oil as such, but that the oils derived from them are derived from organic matter contained in them. All the identifiable matter consists of plant matter or plant degradation matter. No animal matter has been recognized. The larger part of the organic matter consists of spores, the proportion of spores varying in different shales and in different strata of the same shale. A considerable amount of cuticular matter and some woody degradation matter is also present, but little or no resinous matters have been recognized.'

He also says that the Scottish shale is very similar to the Devonian shales of the eastern part of the United States.

> 'While the same kind of constituents comprise this shale, they are present in somewhat different proportions. . . . The shale also contains a slightly larger number of larger resinous-appearing dark-brown bodies of a roughly rounded shape. The larger spores, of which there are several kinds, are of different form and sculpturing, and hence are of different species than those of the Illinois shale.'

Conacher [5, 1917], following the examination of some 200 microsections of various Scottish oil shales, concluded that the animal remains have not contributed to the oil yield. The yellow bodies of the organic matter are a characteristic feature in nearly all the materials which yield oil comparable with that from the shales of the Lothians of Scotland. These yellow bodies are associated with opaque amorphous matter in varying proportions, and the greater the percentage of yellow bodies the higher is the yield of the oil, while as the proportion of opaque matter becomes larger the greater is the specific gravity of the oil produced by distillation. To this the writer adds the observation that the solubility of the organic matter of the shales in petroleum solvents generally increases with the proportion of opaque material present in the shale. Conacher states that in the shales of the Lothians the typical opaque matter is absent and is apparently replaced by carbonized vegetable fragments. He believes that this material yields the tarry products of distillation, some paraffins, and perhaps the bulk of the nitrogenous compounds. The yellow bodies are the source of the typical shale products.

Conacher, after discussing the various theories of the nature of the yellow bodies, concludes that these bodies are simply grains and fragments of resin, and that the supposed cell structures are merely the effects of the physical and mechanical processes of geology.

He cites the experimental evidence of many investigators in support of his conclusions that oil shales and torbanites are derived from the same mother substance as coal 'by the action of natural processes which segrate the resultant resin portions and alter them dynamically'. The altered resins yield paraffins and olefins, while the remains of the cellulosic parts of the vegetable matter yield products more characteristic of coal tar. He believes that the oil shales of the Lothians 'accumulated as the widespread mud-flats of an estuary, and apparently the river which carried the mud brought also a proportion of extremely macerated vegetable matter, and the ebb and flow of the tide would aid in the elimination of the woody materials and the concentration of the resin'. Resinous matter, such as spores, may also play a subordinate part as an oil-yielding material. In his summary he concludes that the oil-yielding matter of the shales he examined is resin and that the nitrogen is present wholly or mostly in vegetable debris other than resin; that there is no evidence to support the theory that petroleum has played any part in the origin of either torbanites or the typical shales of Scotland, or the canneloid shales of the coalfields.

H. M. Cadell [4, 1925] agrees generally with Conacher and feels that it has been clearly established that the oil-yielding material is mostly of vegetable origin, 'derived from the waste of plants growing on the land and not from seaweeds or algae as some authorities have endeavoured to prove, or from animals that lived in the water'. Cadell disagrees with the theory of 'inspissation' and is unable to see how 10 to 20% of mineral matter could absorb and hold 80 to 90% of inspissated petroleum, as would be the case if torbanite were so formed.

Maier and Zimmerly [12, 1927], in studying the chemical dynamics of the transformation of the organic matter of oil shale into bitumen, determined that the transformation reaction, or series of reactions, is of the first order and, since there is no tendency to revert, the evidence is strong that the bitumen is not the same as the unconverted oil-yielding material (kerogen) and that oil shales are not shaly material containing absorbed hydrocarbons.

Critical analysis of the work of the above and other investigators tends to substantiate the theories that oil shales consist of the remains of vegetable matter deposited with mud or silt under water with subsequent alteration caused by decay and solidification, in which the more resistant parts of the plants suffered the least change; that lean oil shale on the one hand and rich torbanites or cannel coals on the other, represent the ends of a series showing gradual transition from one to the other; and that petroleum played no part in the origin of materials usually regarded as oil shales. Physical evidence in the field confirms the latter belief: the close juxtaposition of thin strata of alternating lean and rich shale in which the chemical composition of the mineral matter is substantially the same hardly gives credence to the belief that the migration and subsequent inspissation of petroleum formed the organic part of the oil shales. It is true that shale-like deposits exist in which oil occurs as such. A good example is the diatomaceous shales of the Monterey formation of California, the mineral part of which consists of the skeletons of diatoms from which the oil probably originated. These deposits are not at all like the so-called true oil shales, are easily differentiated from them, and evidently originated in a quite different manner.

Additional evidence as to a possible mode of origin of oil shales was furnished the writer in 1923 by Mr. A. C. Thomson of the Pumpherston Oil Company of Scotland in a private communication, which is summarized below.

At Taubate, about 50 miles from Sao Paulo, Brazil, a shale was worked for some time. About 5 miles from the working, a very marshy area extended for two-thirds of a mile on each side of the river. When Mr. Thomson examined this marsh it was well covered with vegetation (lichens), and in muddy pools on it were live fish. In nearly dry pools fish were dead in the mud. In exposures behind this level place soft, damp, but well-laminated shales had been noted, and to obtain information as to how they may have been formed, a pit was sunk in the marsh to a depth of 20 ft., passing through alternate beds of black and brown mud. At 16 ft. below the surface distinct lamination began, and between the laminations a few well-defined fish fossils were found, showing exactly the same structure as those found in the river. The black mud was deposited when the vegetable growth was of long duration and probably eventually formed oil-yielding shales. The brown mud would form the brown earthy ribs always found in shale beds and was deposited during a period of water overflow. When the water receded, vegetable growth would again begin.

Composition of Oil Shale

The foregoing discussion indicates that the composition of both the organic and inorganic constituents differs in different oil shales. The variability of the organic matter is shown by microscopic evidence and by the fact that different shales yield oils of a wide range of properties when they are retorted under conditions as nearly as possible identical. The oil-yielding substance or substances in oil shale has for years been given the name 'kerogen', though many writers have misapplied the word, using it in such a way as to indicate that kerogen is a definite chemical substance. Analysis shows that the oil-yielding part of oil shales is a complex mixture containing carbon, hydrogen, nitrogen, and sulphur in varying proportions with the carbon-hydrogen ratio as low as 6 to 1 in some shales and as high as 10 to 1 in others.

More precise data are available as to the composition of the inorganic part of oil shales. Table I, taken from U.S. Bureau of Mines Bulletin No. 210, gives the analysis of the ashes of several typical oil shales.

It is to be noted that calcium and magnesium exist in the raw shale mostly as carbonates, and, as Table I shows, there is a striking difference between shales as regards these alkaline constituents.

The nitrogen content of oil shales ranges from a trace to over 1% and is the source of both the ammonia which can be recovered as a by-product of retorting and of the nitrogen bases in the shale oils which cause the characteristic odour of many of the oils. Ammonia, recovered as the sulphate, is the product which saved the Scottish shale oil industry from extinction when it was early faced with the competition of cheaply produced petroleum from other countries. In general, for any particular deposit of oil shale, the nitrogen content varies directly with the oil yield, although in many of the Scottish shales the variation appears to be inverse. With the shales of the United States the direct relationship is almost linear.

TABLE I

Analysis of Ash of Various Typical Oil Shales

Shale	SiO_2 %	Al_2O_3 *and* Fe_2O_3 %	CaO, %	MgO, %	*Total* %
Scotland, good average . .	55·6	34·77	1·55	Trace	100·73
Scotland, Broxburn seam . . .	49·72	35·6	2·4	2·20	89·92
Norfolk, England .	49·5	30·5	11·7	1·2	92·9
Australia, kerosine shale . . .	29·6	67·4	1·4	0·3	100·63
Casmalia, Cal. Monterey shale .	75·8	19·1	1·4	0·9	97·2
Juab, Utah . .	50·4	20·9	14·8	6·8	92·9
Elko, Nevada .	65·5	25·5	0·6	0·8	92·4
Clay City, Kentucky	52·0	19·1	12·5	8·2	91·8
De Beque, Colorado	48·8	17·9	16·6	8·6	91·9
Dragon, Utah .	45·8	16·4	23·9	7·9	94·0
Ione, California .	43·0	38·1	8·7	2·5	92·3
Green River, Wyoming . .	38·9	12·4	38·3	4·9	94·5
Soldier Summit, Utah . . .	44·8	17·1	23·9	5·4	91·2

Oil shales usually contain sulphur in the form of pyrite, calcium sulphate, and other inorganic forms, but most of it is present in the organic matter, and, as a result, shale oil always contains chemically combined sulphur. The gas produced when oil shale is retorted invariably contains hydrogen sulphide, several samples having as much as 5% of this compound. In general, the shales rich in sulphur yield oils with high sulphur content. Oil from the typical low-sulphur (0·35%) Scottish shales contains about 0·3% of sulphur, while the typical Green River shale of Utah (total sulphur 2·2%) yields an oil containing 1·9% sulphur. Commercial consideration will always regard the percentage of sulphur in the oil produced, since sulphur in oils is difficult and expensive to remove in refining.

Nature of Oil Shale Distillation

Although most of the material regarded as oil shale contains appreciable amounts of organic matter soluble in such solvents as carbon disulphide and carbon tetrachloride, the greater part of the organic material is not soluble, and with some typical shales such as those of the Scottish Lothians, the solubility is quite small. The extracts are not oil but rather asphaltic or waxy, solid or semi-solid, materials. Most of the organic matter, or kerogen, when it is heated, undergoes a series of changes which first convert it into a soluble form, and this in turn, with further heating, breaks down, or 'cracks' into oil, fixed gas, and carbon. The kerogen of itself has no commercial value, but heat breaks down this complex mixture of altered vegetable remains and produces from it the more simple gaseous, liquid, and solid hydrocarbons and hydrocarbon compounds that are more or less similar to those obtained from oil-well petroleum.

In this brief discussion of the mechanism of the conversion of the organic matter of oil shale into oil, the writer has purposely avoided the use of words which have been coined to distinguish types of paraffinic, bituminous, and asphaltic matter otherwise not classified except by physical appearance and such properties as solubility in organic solvents. Such words are convenient to use, but often lead to confusion when they are applied to materials not precisely identifiable.

Regardless of the exact composition or nature of the organic matter in different shales, that in all the shales studied by the writer appears to behave in the same general way when it is subjected to heat: the original largely insoluble organic matter changes into a different type of material, soluble in such solvents as carbon tetrachloride, with the evolution of some fixed gas; then, as heating continues, the soluble matter breaks down into gas and oil. The series of reactions is on the whole endothermic, although at certain stages heat apparently is evolved.

Perhaps the most precise quantitative determinations of these transformation reactions have been made by Maier and Zimmerly [12, 1924], whose studies, however, were confined to one particular shale of the Green River formation of Utah. Their first studies were made by heating shale samples in open tubes at various temperatures and for various lengths of time, then extracting the cooled samples with carbon tetrachloride. They found that, as heating at a definite temperature continued, the amount of soluble matter formed reached a maximum and then began to decrease. This indicated that a secondary decomposition or transformation was taking place, that the latter became predominating when the first reaction was nearly complete, and that the products of the secondary reaction were volatile. Later studies in which the samples were heated in sealed tubes made it possible to determine the rates of conversion of the original organic matter into the soluble primary decomposition product and of this primary product into oil and gas. These rates were expressed as logarithmic curves from the equation $dc/dt = KC$ in which dc/dt is the rate of decomposition of the organic matter, and C its concentration in the sample at time T. For the primary reaction, K ranged from $7{\cdot}36\times10^{-4}$ at 275° C. to $9{\cdot}68\times10^{-2}$ at 365° C., where K is rate of conversion in per cent. per hour. A curve in which the logarithm of reaction velocities at various temperatures was plotted against the reciprocal of time, resulted in the equation

$$\log_{10} K = -9{\cdot}075\times10^{3}(1/T)+13{\cdot}46.$$

Some oil or secondary decomposition product was formed at 365° C., and K for this temperature does not lie on the curve determined from observations at lower temperatures. At temperatures above 365° C. the rate of oil formation increased rapidly with rising temperatures. At temperatures below 275° C. the reactions proceeded so slowly as to be immeasurable within reasonable time. No primary decomposition product was formed in 90 days at 100° C. By extrapolation of the reaction-velocity curve, it was calculated that $8{\cdot}4\times10^{5}$ years would be required for 1% of the original organic matter to be converted into soluble primary product at 100° C.

It is obvious from this work that the formation of the primary product is a function of temperature and time of heating. It is probable that reaction rates differ for different shales and may be influenced by the nature of the inorganic part of the shale. It is emphasized that the so-called reaction is probably not a single definite reaction any more than that the organic matter is a simple definite chemical compound; the determined rate is the average of a group or series of reactions, all of the same general nature. Further, all evidence is to the effect that the reactions are of the first order and consequently there is no tendency to revert. This is strong evidence that the primary product is not the same as the original organic matter and that oil shales are not mineral matter containing adsorbed hydrocarbons.

Further studies indicated that at relatively high temperatures, oil and gas formed from the primary product as rapidly as the primary product formed, and that the 'oil' produced from the shale under these conditions was probably a solution of primary product in more or less oil, and that the more rapidly this 'oil' was produced the smaller was the percentage of real oil or secondary decomposition product in it. On the other hand, if the reactions progressed slowly and over a long period of time, the recovered product was a true oil containing little of the primary product. In small-scale tests, by varying the temperature and time of heating in small sealed tubes provided with a collecting chamber below the shale sample, a complete series of oils was produced from the same oil shale. These oils in physical appearance ranged in nature from the dark-coloured viscous materials similar to typical naphthenic crudes, on the one hand, to a fluid, light-coloured relatively volatile product containing much paraffin wax and more typical of the paraffin-base crudes, on the other.

It is regrettable that these investigators were not able to continue their investigation or more thoroughly to examine the products made in their small-scale studies. The results of this admittedly incomplete study strongly suggest how petroleums of unlike character may have been formed from the same kind of oil shale, thus rendering unnecessary the additional theory that they were altered by filtration in migrating from the point of origin to reservoir structures, feasible though this latter theory may be. The work also emphasizes the fact, confirmed by large-scale experimental studies, that the quality—and yield—of oil produced from a given shale is determined to a considerable degree by the manner in which it was produced from the shale. Add to this the fact that the organic matter in different shales is of varied composition and the observation that different shales yield oils of greatly unlike quality is easily understood.

That different shales yield oils of different quality when the shales are retorted under as nearly as possible identical conditions as to rate of oil production is shown by Table II:

TABLE II

Comparison of Oils Produced from Different Oil Shales

Source of Shale	*Oil yield U.S. gal. per 2,000 lb.*	*Specific gravity of oil*	*% of crude distilled to 275° C.*	*Unsaturates in distillates to 275° C.**	*Setting-point of crude oil†*
Soldiers Summit Utah	49·7	0·894	37·2	36·9	28·5
Grand Valley, Colo.	36·7	0·899	38·5	42·8	25·0
De Beque, Colorado	45·3	0·897	34·8	39·8	27·5
Elko, Nevada	63·2	0·866	36·7	33·3	35·0
Kentucky	16·0	0·934	40·9	44·2	0
Brazil	118·7	0·870	40·5	33·6	19·0
Australia	121·8	0·867	40·2	26·9	18·5
Scotland	17·7	0·872	37·6	23·8	33·0
Utah, Coal	33·6	1·002	38·0	47·8	32·0

* Percentage soluble in excess of 98% sulphuric acid under definitely specified conditions.

† An arbitrary method of determining the melting-point of the oil.

As an indication of how the quality of oil produced from a given shale is influenced by the conditions of production, the following tabulation shows the yield and nature of oil produced from a Colorado oil shale in an experimental retort under conditions such that in one case oil was produced 5 times as rapidly as in the other:

Rate of oil production, c.c. per min.	1·0	0·2
Yield of crude oil, gal. per ton	36·9	35·5
Specific gravity of crude oil	0·913	0·901
Viscosity of crude oil—Saybolt sec. at 130° F.	53·0	50·0
Percentage of sulphur in crude oil	0·60	0·53
,, of nitrogen in crude oil	2·07	1·79
,, distilled from crude oil to 150° C.	7·6	9·5
,, distilled from crude oil to 200° C.	16·8	19·6
,, distilled from crude oil to 275° C.	34·8	39·0
Melting-point of crude oil ° F.	72·0	79·0
'Unsaturation' of distillate to 275° C., %	44·4	39·1

The following conclusions have been drawn from much experimental evidence:

1. The quality of oil produced from a given shale is largely a characteristic of the particular shale.
2. The yield of oil from a given shale increases with the rate at which the oil is produced up to a certain maximum. If rates higher than those which yield maximum quantities are attempted, overheating will decompose the oil, decreasing the oil yield and increasing the yield of gas.
3. The quality of oil produced from a given shale, as indicated by relatively low specific gravity, relatively high volatility, and relatively low percentage of 'unsaturates', improves as the rate of oil production decreases.

The evidence leading to these conclusions strongly suggests that most shale oils are really mixtures, in varying proportions, of (*a*) primary decomposition products of the organic matter of the shale, and (*b*) oils resulting from the cracking or further decomposition of the primary product.

As further evidence of this belief is the fact that if, at any given rate of oil production, steam or an inert gas is passed through the distilling shales, the oil produced is lower in quality and higher in yield than if the steam or gas were not used. The steam evidently lowers the distilling temperature of the primary product by reducing its partial pressure in the mixture of gas and vapours, consequently the primary product has less opportunity of decomposing in the retort and more of it is recovered in the condensed oil.

Observations in the field and of specimens of certain shales indicates that the process of conversion of original organic matter into primary decomposition products takes place in nature under certain conditions. Where shale deposits have been subjected to stresses that have caused local distortion, it is usual to find in the shale, nodules or lenses of bituminous matter soluble in carbon tetrachloride and closely resembling the primary decomposition products produced in the laboratory. The naturally occurring hydrocarbon gilsonite, which some investigators regard as similar to the primary decomposition product, evidently originated in deposits of Green River shale, now almost barren of organic matter, and was deposited in vertical fissures above the shales. One exposed section in Utah shows the bottom of the gilsonite deposit stringing out in small veinlets which apparently terminate in the probably once oil-yielding shales.

The rate of oil production also is of practical value in connexion with the distribution of nitrogen (and possibly sulphur) between the oil and the spent shale. When the oil is produced rapidly from the shale, more nitrogen appears in the oil and less in the spent shale than if the oil is produced slowly. Likewise, with rapid oil production, there is less fixed carbon in the spent shale than with slow oil production. Consequently, if it is desired to produce a maximum amount of ammonia as a by-product from the shale, slow oil production is indicated, since the nitrogen in the oil is in the form of complex nitrogen bases, which can readily be removed from the oil but would require further processing to be converted into ammonia, while if the spent shale is heated to approximately 1,200° F. and treated with steam, the greater part of the nitrogen can be recovered as ammonia. This method is used in the Scottish shale-oil industry where ammonia has been a most valuable by-product.

Laboratory studies, small-scale and semi-commercial retorting experiments, and full commercial production, though not yet well correlated, convincingly show that each particular oil-shale deposit is likely to present its own retorting problems. These problems relate to the physical behaviour of the shale in mining, crushing, and retorting, as well as the general nature of the oil produced and how the oil and the products made from it can be modified by the conditions of retorting or subsequent treatment of the oil.

Mining, handling, and crushing are not discussed here, but they present practical problems for the industry. The writer has learned as the result of somewhat limited experience in mining and handling shales that the varied experience of the metal miner will be of great value in the working of oil shales, whereas it has been generally believed that oil-shale mining methods will usually closely resemble present-day coal-mining methods. Many oil shales have coking characteristics somewhat like typical coking coals. This property seems to be inherent in shales from certain localities, and cannot be correlated in general with richness. Lean shales seldom show coking tendencies, and whereas many quite rich shales do not coke, others from different localities, and not so rich, coke so strongly as to make impossible their retorting in a continuous process without admixture with leaner shales.

The manufacture of shale oil is described elsewhere in this treatise by another writer, but it may be pointed out here that the future shale-oil industry may depart widely from what has been practice in the past. Just as oil shales differ, so do the products made from them, and the nature of the final finished products is influenced by the methods used in manufacturing the crude oil.

Oil shale is regarded as a source of supply of hydrocarbon oils, to be drawn upon to supplement or largely supplant petroleum when the demand for petroleum products becomes greater than can be supplied by the natural deposits of petroleum. Other than hydrocarbon oils, by-products of more or less interest and importance can be obtained from oil shales. The usually considered by-product is ammonia, but ammonium compounds are now produced so inexpensively from other sources that this by-product is not likely to be as important as in the past. It is not improbable that in future the nitrogen bases present in all shale oils will be of more value to the industry than any ammonia that can be produced.

The writer has previously likened the production of shale oil to the concentration of a valuable mineral from a low-grade ore. In an industry of this nature it is not usual to begin to refine the mineral until the concentrate has been reduced to the lowest practicable bulk. The primary operation is to eliminate the waste matter or gangue and dispose of it as quickly and cheaply as possible.

In shale-oil production, the oil is the desired concentrate, the spent shale the gangue. Inasmuch as rapid concentration or production of the oil leads to an oil of relatively inferior quality, many have felt that rapid oil production from shale by relatively high-temperature retorting aided by 'carrier' gas or steam is not practical, but actually the inferior grade of oil so produced can be made to yield all the desired products of slowly produced crude oils by subsequent 'cracking' in apparatus operated independent of the oil-shale retort. Regarded in this manner, the retort becomes the concentrating device, by means of which the desired concentrate—crude oil—is produced as rapidly as possible, and the relatively expensive retorting equipment is not employed as a partial refining device which, when so used, limits its capacity and therefore increases the cost of the crude product. Two thousand pounds of oil shale will yield, for example, 320 lb. of oil (about 40 gallons to the ton from a relatively rich oil shale). This amount of oil may be produced from the retort in 1 hour, or about the same amount of a materially superior oil can be produced from the same ton of shale in 6 hours, but meanwhile the concentrating capacity of the retort has been reduced to a sixth of the capacity it had in the first operation. It is evident that an auxiliary cracking unit will represent a lower capital investment and cost less to operate than the additional retorting equipment required to produce, directly from the retorts, oils of equivalent quality to those made by a process of rapid retorting followed by a secondary distillation or 'cracking' of the crude oil.

Except where long-time treatment of the shale is required to produce particular by-products, such as ammonia, from the shale, or to impart to the spent shale properties that will be commensurate with the cost of long treating time, the writer pictures the future oil-shale industry as one in which the retorting equipment will produce oil as rapidly and at as high a temperature as feasible. The oil so produced will go to the refinery to be improved in quality and finally, or simultaneously, fractionated into raw distillates for refining into commercial commodities.

The shale oils must also be regarded as future sources of valuable by-products. The crude oils and distillates contain nitrogen compounds of possible value. Oils and gases also contain hydrocarbons and hydrocarbon derivatives of the unsaturated series which are now rapidly increasing in importance as raw materials for the synthetic chemist, and future study will show how the yields of these compounds can be increased if desired and their recovery simplified.

While the oil-shale industry is similar in many respects to the coal-mining and coal-distillation industries, it will probably be developed by the petroleum industry if it is to reach a position of importance in supplying the world with hydrocarbon oils. The magnitude of the possible future industry may be pictured by assuming the production of 1,000,000 bbl. of shale oil per day from oil-shale deposits that will yield on the average 35 U.S. gal. of crude oil per short ton. To produce this quantity of oil 1,200,000 tons or, roughly, 1,000,000 cubic yards of solid shale would have to be mined, transported, crushed, and handled through retorts every 24 hours, and approximately 1,500,000 cubic yards of broken waste spent shale disposed of. Herein lies an important difference between the petroleum- and coal-distillation industries and the oil-shale industry. The petroleum industry has no solid waste to dispose of except the small amount of coke formed by cracking, and coke is a valuable fuel. The coal-distillation industry yields a solid residue—but this again is coke, highly useful in industry. The residue of oil-shale distillation, except in few instances, has no commercial value, and for every barrel of oil produced, 1·5 cubic yards of waste must be disposed of.

REFERENCES

1. Ashley, G. H., *U.S. Geological Survey Bull.* no. 659, **11** (1918).
2. Becher, J. J., and Serle, H. B.P. 214 (1681).
3. Bertrand, C. E., and Renault, B. *Bull. Soc. Hist. Nat. Autun*, **5**, 159 (1892).
4. Caddell, H. M., as reported by Bailey, E. M., The Oil Shales of the Lothians, *Memoir Geol. Survey Scotland*, Part III, 3rd ed., 165 (1927).
5. Conacher, H. R. J. *Trans. Geol. Soc. Glasgow*, **16**, part 2, 164 (1917).
6. Cunningham-Craig, E. H. *J.I.P.T.*, **2**, 238–69 (1916).
7. Davis, C. A. *U.S. Geol. Survey Bull.* no. 641, 163–5 (1917).
8. Eele, Martin, Hancock, Thos., and Portlock, Wm. B.P. 330 (1694).
9. Gavin, M. J., Oil Shale: U.S. Bureau of Mines Bulletin no. 210 (1924).
10. *Gillespie* v. *Russel.* Court of Session 1854–6–7.
11. Jeffery, E. C. *Econ. Geol.* **9**, 735 (1914).
12. Maier, C. G., and Zimmerly, S. R. *Bull. Univ. Utah*, **14**, no. 7, 62–81 (1924).
13. McKee, R. S., and others. *Shale Oil* (1925).
14. Robertson, J. B. *Proc. Roy. Soc. Edinburgh*, **34**, 190–201 (1914).
15. Scheithauer, W. *Shale Oils and Tars and their Products*, 12 (1913).
16. Selligue, A. F. F.P. no. 9467 (14 Nov. 1838; addition 27 March 1839).
17. Steuart, D. R. *Memoir Geol. Survey Scotland*, Part III, 2nd ed., 164–5 (1912).
18. Thiessen, Reinhardt. *Econ. Geol.* **16**, nos. 4 and 5, 289 (1921).
19. Young, James, B.P. 13,292 (17 Oct. 1850).

OIL SHALE; OCCURRENCE AND GEOLOGY

By H. R. J. CONACHER

THE oil shale worked on a large scale in the Lothians of Scotland is the typical material. While the term 'oil shale' is precisely applicable to it, commercial practice has expanded its meaning to include all manner of materials from which mineral oil can be obtained by distillation. Consequently it is now applied in a number of cases which lithologically are not shale and which differ from the Scottish type also in the nature of their organic matter and, consequently, in the character of the oil obtainable from them. The range in lithological types is shown by the following table, which gives the percentage and composition of ash from certain examples, while the variety in the character of the organic matter is indicated by particulars of yield, &c., of crude oil when tested under comparable conditions.

	Normal shale [1]	*Scottish (Lothians)*		*Boghead, Scotland* [2]		*Torbanite, N.S.W.*			*Tasmanite, Tasmania* [6]	*Kukersite, Estonia* [7]		*Casmalia, California* [8]	*Green River, Colorado, Utah, &c.* [8]
						[3]	[4]	[5]					
Approximate % of ash . .	..	80	80	20	..	20	..	..	70–6	32	..	..	51–65
Composition of ash:													
SiO_2 . .	60·15	56·45	47·60	56·00	58·31	29·643	93·0	48–77	68–73	28·8	30·8	75·8	39–49
Al_2O_3 . .	16·45	21·10	22·24	43·52	33·65	64·397	3·5	5·22	12–16	6·8	10·7	19·1	12–19
Fe_2O_3 . .	4·04	15·90	10·90	0·35	7·00	3·050	*	..	6–7	7·2	5·5		
FeO . .	2·90	..	..	..	..	..	..	..	..	..	..	..	..
CaO . .	1·41	2·23	1·60	trace	..	1·438	*	..	0·5–4	42·9	40·1	1·4	17–38
MgO . .	2·34	1·90	1·62		..	0·250	*	..	1·5–3	1·8	1·5	0·9	5–11
Na_2O . .	1·01	1·21	1·37	0·36	0·41	0·355	0·50	..	0·5–1	3·6	3·7	..	..
K_2O . .	3·60		1·92	0·40	0·84	0·748	1·75	..	2·5–3				
CO_2 . .	1·46	..	..	..	..	..	..	..	..	..	..	..	..
SO_3 . .	0·58	..	2·48	..	..	..	..	..	0·5–2 SO_2	9·3	7·9	..	..
C . .	0·88	..	..	..	..	..	..	..	..	..	..	..	..
S . .	..	1·27	..	..	..	..	..	..	..	..	..	..	..
Yield of oil, gal. per ton . .	..	25		100		100	..	..	33–38	25–78	..	10–50	20–60
Sp. gr. . .	..	0·870		0·880		0·880	..	..	0·935	0·970	..	0·960	0·920

Authorities for analyses of ash:

1. F. W. Clarke, *Data of Geochemistry*, 1924, p. 552.
2. Evidence in Jury Trial, *Gillespie* v. *Russell & Son*, Edinburgh, 1853.
3. J. E. Carne, *The Kerosene Shale Deposits of New South Wales*, 1903, p. 272.
4. New South Wales Dept. of Mines, Sydney, 1935.
5. J. R. M. Robertson, 'The Occurrence of Torbanite or Kerosine Coal in the Colony of New South Wales', *Min. Inst. Scot.* **14,** 88–126 (1892).
6. Tasmanian Geol. Survey, *Mineral Resources*, **8,** ii. 13 (1933).
7. Kogerman, *On the Chemistry of the Estonian Oil Shale 'Kukersite'*, Oil Shale Research Laboratory, Tartu, Bulletin no. 3, 1934.
8. M. J. Gavin, *Oil Shale*, U.S. Bureau of Mines Bulletin 210, 1924, p. 29.

* Present, but quantity not determined.

Shale of the Lothian type grades mainly, by reduction of mineral matter, into torbanite, and by variation in nature of organic matter into 'mussel-band' shales and cannel coal. Other types such as Tasmanite, the Kimmeridge Blackstone, the Green River shales of Colorado, Utah, and Wyoming, &c., form unrelated groups outside the series.

There are few regions of the world which do not contain material of one or other of these types, but only the outstanding occurrences can be dealt with here.

Shales of the Lothian type yield only traces of soluble matter to organic solvents, the oil obtained on distillation being derived from organic matter by thermal decomposition. E. M. Bailey (*Oil-Shales of the Lothians*, p. 169, 1927) reports a maximum of 0·98% obtained by 12 days' extraction with carbon disulphide and chloroform as compared with 2·41% obtained from Colorado shale by Gavin and Aydelotte, this representing 18·22% of the yield obtainable by distillation. (U.S.B.M. Bulletin 210, p. 28, 1924.)

The Scottish shales in their unweathered state are black or very dark brown rocks, possessing fine lamination which is most strongly displayed by weathered or burnt specimens. They occur in a group of sediments peculiar to central Scotland, the Calciferous Sandstone Series, lying between the Old Red Sandstone and the Carboniferous Limestone. In Mid and West Lothian the series has a thickness of about 5,000 ft., but oil shale occurs only in the upper two-thirds, where the sediments consist mainly of sandstone and shale with subordinate beds of fresh-water, sometimes oolitic, limestone. The finer sediments are frequently sun-cracked and occasionally traversed by sandstone dykes approaching 10 ft. in depth and up to about 18 in. in breadth; the sandstones generally consist of angular grains strongly cemented, and occasionally contain oolitic structures. Two or three thin seams of poor coal occur. The workable seams of shale, which range up to 14 ft. in thickness, are the portions richest in organic matter, of much greater thicknesses of dark shale; they differ only in degree from the beds constituting the roof and floor of the workings, and generally are not sharply distinguished from them; they vary in richness from point to point both vertically and horizontally. There are about a dozen seams, but at no locality are all of workable thickness and quality. The area is crossed by two sets of folds and related faults, resulting in severe contortion of the relatively pliable oil-shale seams with development of highly polished planes of internal movement. Igneous dykes and sills of two ages have invaded the series, destroying the shale seams over large areas, and resulting in the presence of free mineral oil and other native hydrocarbons. Most of the individual seams have their own lithological characteristics and also vary in the yield and quality of the oil. Fossils are scarce, the commonest being scattered leaves, cones, and stems of rather small specimens of the Carboniferous flora, with remains of fish (occasionally complete specimens). In a few instances the shale is packed with ostracod shells. Megascopic examination gives little hint as to the nature of the organic matter in the Scottish shales, as the amount accounted for by the visible fossils is altogether inadequate to supply the yields obtained, nor is any one of them sufficiently general in occurrence. Microscopic examination of thin sections shows the presence of extremely macerated vegetable matter, fragments of recognizable tissue, occasional spores and spots of yellow material, and scales and spines of fish on a background of fine mineral grains coloured pale brown or yellow, according to the thickness of the section and the particular seam under examination.

In the adjacent coal-fields, on a higher geological horizon than the true oil shales, various canneloid shales are found which were worked in the early days of the mineral oil industry; these are generally from 1 to 2 ft. in thickness, and were mined in conjunction with coal seams. They frequently give large yields of oil, but the impossibility of refining this to modern standards has made these materials unworkable. They differ from the Lothian shales in their dense black colour, black streak, and coarser lamination; the presence in some instances of great numbers of *Carbonicola*, *Naiadites* and *Anthrocomya*, preserved as ironstone nodules, causes them to be known as 'mussel-band' shales.

At the base of the Coal Measures, separated from the Lothian shales by about 2,500 ft. of sediments, there occurs the Boghead coal or Torbanehill mineral, the type-material of the torbanites and the material originally worked for oil in Scotland. This occurred as one seam with a maximum thickness of 30 in. in an area of about 3,000 acres to the south and west of Bathgate, Linlithgowshire, associated with common coal and ironstone. In different parts of the field it varied in colour from brown to black, the former being the richer, yielding up to 120 gallons per ton of oil having higher refining value. It is tougher than ordinary cannel coal and breaks with difficulty except under an axe. The fracture of the black variety is slightly waxy, showing numerous very minute, glistening points; the fracture of the brown variety is dull, of dark chocolate colour, semi-detached splinters being red and translucent.

The only fossils noticeable in the seam are very scarce fish remains, and prints of leaflets and rootlets; specimens of the black variety are usually penetrated by *Stigmaria*. In thin section this material presents a mosaic of pale yellow bodies in a ground-mass which is only translucent in very thin sections and is then deep red in colour. The individuals in the mosaic show traces of structure, of which numerous interpretations have been presented by different observers. They resemble, but are more definite in form than the yellow spots mentioned as occurring in the Lothian shales, and on account of the connexion which can be made out between their presence and the yield and nature of the oil obtained on destructive distillation they are considered to be the essential items in the constitution of normal oil shales and torbanites. Similar yellow bodies occur in numerous cannel coals and in the cannel shales, but only to a subordinate extent. Torbanite closely resembling that of the Bathgate district occurs about the same horizon elsewhere in Scotland, but in very much smaller quantity, and no other deposit has attained such economic importance as that at Bathgate.

Probably the closest approach lithologically to the Lothian shales is to be found in the shales of Cainozoic age occurring in a limited area near Elko, Nevada. At this locality several seams up to 6 ft. in thickness and yielding as much as 50 gallons per ton for a limited thickness occur in a series of lake deposits associated with rhyolites and white tufaceous sediments. Perfectly fresh specimens are brown, weathering to blue. The principal seam is associated with lignite and contains thin partings crowded with delicate bivalve shells and carbonized seeds.

In Burma, oil shale of Cainozoic age occurs in a basin of metamorphic rocks between the Dawna Mountains and the Siam frontier, east of Moulmein, in country densely clad with jungle. There are half a dozen seams enclosed in a series of greenish and bluish shale and mudstone with sandstone and nodular fresh-water limestone. The freshly mined shale has a rich red colour, but quickly turns black. While good yields are obtainable, the oil is of a type difficult to refine.

Oil shales somewhat approaching the Lothian type also occur in Spain, near Castellon. They are of Cainozoic age and are remarkable for the well-preserved remains of minute insects.

Torbanite of Carboniferous age occurs in France at Autun (Saône et Loire) and Frejus (Var). The deposit at Autun was the subject of the classical studies of Bertrand and Renault. That at Boson is similar, being a black material with brown streak and rough, somewhat glistening fracture. In transparent sections under the microscope it presents a beautiful mosaic of yellow and orange-coloured bodies with well-defined internal structure which has caused them to be ascribed to unicellular algae related to existing species. The torbanite is said to be about 4 ft. thick, and is associated with greater thicknesses of black shale apparently differing only in the relative percentages of ash and organic matter. Typical shale of Miocene age also occurs in the Basses Alpes at Bois d'Asson.

In Bulgaria (Bresnik district) materials occur which have been described as torbanite, but hand specimens and thin sections indicate a fine-grained limestone containing some minute plant fragments and soaked with oil. The series is considered to be of Jurassic age, and is very steeply folded.

Torbanite also occurs in the eastern United States, particularly in Kentucky, but the most remarkable series of occurrences is in New South Wales. In that State many detached areas are known, each containing a single seam up to about 4 ft. 6 in. thick. Most of these deposits occur at about the same horizon in the Greta Coal Series of the Kamilaroi (formerly Permo-Carboniferous). Each deposit is lenticular and may pass into common coal either vertically or laterally, and frequently becomes hard and stony for a few inches at the top and bottom. The enclosing beds are generally grey, sandy shales. The material from many of the deposits has particular characteristics by which it can be identified. Typical specimens from the Wolgan-Capertee area are black with rough conchoidal fracture showing many glistening points; the bedding is discernible by its dull surface when split open, by the greater ease with which the material can be split in that direction, and flattening of the particles in the direction of the bedding is revealed by close examination with a lens. On weathering, the surface becomes duller, and in the course of 20 years may develop a noticeably grey crust which apparently consists of the ash left by removal of the organic matter. Ultimately weathering may penetrate deeply into the block, leaving a brown, clayey coat which makes the torbanite extremely difficult to distinguish by eye from the sandstones and sandy shales of the district. The glistening points visible on a clean fracture are found to be minute resinous bodies crossed by the line of fracture, and the roughness of the surface is due to the fracture passing around and not through the greater number of these. Such a fracture is noticeably brightest at the point of impact, becoming rougher and duller as the fracture spreads and tends to pass around and not through the resinous bodies. Specimens from most of the other deposits are black to greenish in colour with a waxy or silky lustre on fresh fractures, this lustre being due to the fracture passing through all the yellow bodies which predominate over the ground-mass. Whereas weathering of specimens from Wolgan attacks the yellow bodies first, leaving a reticulated surface of the ground-mass, the reverse is generally the case. Thus specimens from Hartley Vale show a close-set mosaic of nearly globular bodies with the matrix etched out, and the deeply weathered crust on specimens from Baerami shows the very large yellow bodies quite detached but intact. In some cases the yellow bodies are very large, measuring as much as 0·5 mm. in diameter with a thickness of 0·2 mm. This form is generally characteristic of Australian specimens and in contrast with those from Scotland and France, which are roughly spherical, with radial structure, measuring about 0·1 mm. in diameter. Weathering sometimes proceeds underground, and in such cases the joints in the seam are eroded laterally to the extent of several inches, the space being partly occupied by the loose ash, brown in most districts, but occasionally white or red. The seams vary rapidly in thickness, and the quality also varies laterally as well as vertically, becoming impoverished through increased proportion of ash or changing to common coal, ironstone, &c.; this feature is very well shown in a series of sections appended to the report of the Newnes Investigation Committee. The material is remarkably elastic, and blocks and splinters spring from their beds with considerable force when freed in the course of mining. Recognizable fossils are uncommon, with the exception of vertical stems and whorls of leaves apparently belonging to *Phyllotheca*. The material frequently gives as much as 150 gallons of crude oil per ton of shale.

Within the region of the torbanite in New South Wales there also occur various deposits of hard stony material yielding oil similar in character to that obtained from the normal torbanite, but much less in quantity. They are hard and rather heavy, brown to black in colour when fresh, with rough fracture; their appearance in the field does not usually suggest that they could give the yields they do, but on the other hand thin sections suggest much higher yields than are actually obtained. The seams generally consist of several beds varying sharply in quality, and it appears as if they represent what would have been normal torbanite seams but for heavy contemporaneous impregnation with mineral solution which has had the effect of increasing the weight of inert material without much affecting the appearance in thin section.

On the north coast of Tasmania the very remarkable material known as Tasmanite occurs in the neighbourhood of the Mersey River. The deposit is of approximately the same age as the torbanite of New South Wales, but differs markedly from it. When freshly mined it is grey with a brownish bloom due to immense numbers of yellow resinous disks having a diameter of about 0·45 mm. with occasional larger specimens. They are regarded as spore cases and are embedded in a matrix of very fine sand, being strewn over the bedding planes in dense patches about an inch square and more or less thinly scattered over the remaining surface. Occasionally there are seams up to ½ in. thick and 1 or 2 in. in diameter from which mineral matter is practically absent. Iron pyrites occurs on the joint planes, encrusting fossils, and as small nodules and single crystals scattered along the bedding planes, while sulphur also occurs in combination with the organic matter. Marine shells are distributed throughout the seam, which is also sprinkled with glaciated pebbles ranging from the size of a pea up to boulders of 100 cu. ft. Patches of corroded crystals, apparently pseudomorphs of glauberite, also occur and have the appearance of having been drifted into position. There is but one seam of this material, having a thickness of up to 6 ft. with a 2-ft. bed of poorer material in the middle. The seam differs only from the enclosing sandy mudstones in the presence of the spore cases which are only very thinly distributed in the overlying and underlying beds, and in adjacent districts its position appears to be occupied by coal. On weathering, the spore cases turn brown and assume a saucer shape through the curling up of their edges. They differ from the spore cases so commonly met with in coals and associated rocks elsewhere in the absence of the triradiate ridge and micropyle. In thin section they show fine banding parallel to the outer surface and numerous well-defined punctures. The latter appear to be unevenly distributed, generally taper slightly inwards and may be interrupted, but these puzzling features may be partly due to their being invisible unless infiltered by mineral matter. They closely resemble the bodies characteristic of the New Albany shale in the eastern United States.

The New Albany shale (also known as the Chattanooga or Ohio) of the eastern United States is of Devonian age and outcrops over a very long area extending from Alabama to the Great Lakes. As seen in Kentucky it consists of rather stony black shale which seems to contain a good deal of iron. The bedding planes are strewn with minute plant fragments, among which can be distinguished a sprinkling of spore-like bodies, and a few *Lingulae*. In thin section the minute spore-like bodies show similar characteristics to those found in Tasmanite; characteristically their diameter is only about 0·15 mm., but specimens measuring as much as 0·25 mm. occur in northern localities. The series has a thickness of about 100 ft. and little variation in richness is noticeable throughout the section, the general aspect of which, both in the field and in thin section, is that of carbonaceous shale. Generally the yield is under 10 gallons per ton.

The high plateau country of Utah, Colorado, and Wyoming, having an area of several thousand square miles, is formed of a mass of calcareous shales which is over 2,000 ft. thick in some districts. Almost the whole of this mass yields some oil on distillation, but the richest zones occur about 600 to 1,200 ft. from the bottom, the chief of which is known as the Mahogany Seam. This series of limestones is of Green River (Cainozoic) age, resting conformably on the Wasatch beds which overlie the Cretaceous

Mesa Verde. The poorer beds are pale brown on fresh fractures, turning white on prolonged weathering; the richer beds are a deep red colour, blackening on a few hours' exposure and generally weathering with a white crust through oxidation of the organic matter, but sometimes the mineral matter is leached out, leaving the organic matter in flexible sheets like a stack of brown paper. The richest specimens give a silky cross-fracture resembling that of some torbanite, but scrutiny shows that the glossy surface is not made up of numerous glistening points but of minute parallel streaks, even the richest beds consisting of minute alternations of rich and poor sediment. Prints of aquatic insects up to 1¼ in. long sometimes occur thickly strewn on the slabs, which are often finely ripple-marked and rain-pitted; in some localities fossil fish are common, and towards the base some beds are packed with ostracod shells. The whole series has been very closely studied by the U.S. Geological Survey and is described in a series of Bulletins and Professional Papers which arrive at the conclusion that the oil yield is derived from vegetable matter, largely algal, but both field and laboratory examination give the impression that at least a great part of the oil is already present in that form, whatever its ultimate source may be (cf. results of extractions quoted on p. 3100). Free oil occurs in porous oolitic beds throughout the series and also in the empty casts of salt crystals, while the rich beds smell of oil on fresh fracture or when exposed in the sun. Solid native hydrocarbons also occur abundantly ranging up to the huge 'Cowboy' and 'Bonanza' veins of Uintaite, up to 18 ft. in thickness and traceable for 8 miles.

The Kimmeridge clay which occurs over a large part of England and in parts of France is generally of a dark bituminous nature, weathering to mud rather readily, but at Kimmeridge on the Dorset coast parts of the series are so rich in organic matter that they have been used as fuel for centuries under the name of Kimmeridge coal. On distillation these beds give substantial yields of highly sulphurous oil. The richest of these zones is the 'blackstone', about 4 ft. thick, the best specimens of which show a waxy cross-fracture with a brownish tinge. The bedding planes are rather rough and strewn with fragments of marine shells, many of which are coated with iron pyrites. Much sulphur is also present in organic combination. Fair yields are also obtainable from a considerable thickness of strata above the blackstone seam, and a relatively rich bed known as 'short-joint coal' occurs 25 ft. above the main seam.

Another material of marine origin is kukersite which occurs near the south coast of the Gulf of Finland, in Estonia and Russia. It is of Ordovician age, and notwithstanding its great antiquity it has a remarkably recent aspect as, lying on the Baltic Shield, it has been practically undisturbed since its accumulation. The kukersite is a buff-coloured, clayey material, containing abundant remains of polyzoa, trilobites, &c., and it occurs as thin beds between rather nodular limestones. The beds for 20 or 30 ft. above and below are also limestone with some partings of inferior kukersite. The yield of oil is as much as 80 gallons per ton. The oil has little resemblance to that from any other material.

In South Africa oil shales occur in the Ecca Coal Measures and in the Stormberg Series of the Karoo System (approximately Permian) of Natal and the Transvaal, exposures being known throughout a belt about 250 miles long stretching from Ermelo in Transvaal to Impendhle in Natal. They are frequently described as torbanite, but are really sandy black shales with prominent flakes of mica. The streak is generally dark brown and the fracture coarse and rough. Yields are generally about 30 gallons, but may be as high as 70 gallons per ton. The seams are generally thin—under 2 ft.—but are associated with a greater thickness of coal.

The Albert Shale (Devonian) of New Brunswick and Nova Scotia yields oil to some extent throughout its entire thickness of 6,000 ft. The series contains the remarkable vein of Albertite and the basal conglomerate contains enough oil to flame freely in a fire. There are several well-defined seams, but the richest beds are the so-called 'curly' seams. These are hard, tough materials smelling strongly of oil when broken. On fresh fracture they have the appearance of 'watered' silk through the presence of intensely contorted alternations of brilliant black and dull, dark brown layers. Notwithstanding the appearance of intense movement slickensides are not developed, but frequent small jet-like veins traverse the material sometimes following, but as frequently transgressing, the lamination. The appearance of the material strongly suggests turbulent flow of a highly viscous mass, but thin section shows it to contain recognizable vegetable remains—spore cases, carbonized tissue—giving signs of disruption and arranged as if in lines of flow, with coarse, angular, mineral matter. The oil obtainable is heavy and asphaltic.

In the Oligocene coal series of Fushun, Manchuria, the thick coal seam is overlain by a rather carbonaceous shale giving only small yields of oil (10–15 gal.), but which is distilled, as it has to be handled in the course of mining the coal. The shale is almost black, heavy, and fairly hard.

In California some attention has been paid to the Monterey shale (Middle Miocene) at its outcrop in Santa Barbara county to the west of the Santa Maria field where it forms the oil 'sand'. It is a brown to black, massive material, irregularly jointed, the faces slightly grooved by movement and coated with asphalt. Its thickness is said to vary from 400 to 1,700 ft. The yield varies from about 10 to 50 gallons of oil per ton with a specific gravity about 0·96. Marine fossils occur in the deposit, and thin sections show irregularly distributed diatom frustules associated with tufaceous material, unweathered felspars, &c.

In South America oil shales have been worked a little in the State of São Paulo, Brazil, where they occur as a soft, light deposit, with well-developed bedding planes strewn with fish remains and obscure plant fragments. When fresh the shale is dark, but quickly turns light yellow on exposure. Specimens from near Antofagasta, Chile, consist of limy shale and limestone.

SELECTED BIBLIOGRAPHY

America—Canada and United States.

Bradley, Wilmot H. A Contribution to the Origin of the Green River Formation and its Oil Shale. *Bull. Amer. Assoc. Petr. Geol.* 9, no. 2, 247–62 (March–April 1925).

—— *Shore Phases of the Green River Formation in Northern Sweetwater County, Wyoming.* U.S. Geol. Surv. Prof. Paper 140 D (1926).

Bradley, Wilmot H. *Algae Reefs and Oolites of the Green River Formation.* U.S. Geol. Surv. Prof. Paper 154 G (1929).

—— *The Varves and Climate of the Green River Epoch.* U.S. Geol. Surv. Prof. Paper 158 E (1929).

—— *Origin and Microfossils of the Oil Shale of the Green River Formation of Colorado and Utah.* U.S. Geol. Surv. Prof. Paper 168 (1931).

GAVIN, M. J. *Oil Shale.* U.S. Bureau of Mines Bulletin 210 (1924).

Oil Shales of Kentucky. Kentucky Geol. Surv., Ser. VI, **21** (1925).

WINCHESTER, DEAN E. *Oil Shale of the Rocky Mountain Region.* U.S. Geol. Surv. Bulletin 729 (1923).

WRIGHT, W. J. *Geology of the Moncton Map Area.* Canada, Dept. of Mines, Geol. Survey Memoir 129 (1922).

Burma.

COTTER, G. DE P. The Oil Shales of Eastern Amherst, Burma. *Records of Geol. Surv. of India*, **55**, pt. 4, 273–313.

Estonia.

BEKKER, HENDRIK. *The Kuckers Stage of the Ordovician Rocks of North-east Estonia* (Tartu, 1921).

LUTS, K. *Der Estländische Brennschiefer Kukersit, seine Chemie, Technologie und Analyse* (Tartu, 1934).

France.

BERTRAND, C. EG., and RENAULT, B. Pila Bibractensis et le Boghead d'Autun. *Bulletin de la Soc. D'Histoire Naturelle d'Autun* (Autun, 1892).

Great Britain.

The Oil-Shales of the Lothians, 3rd edition. Mem. Geol. Surv. Scotland, (1927).

Manchuria.

UWATOKO, KUNIO. The Oil Shale Deposit of Fushun, Manchuria. *Journ. Fac. Sc., Hokkaido Imp. University* (1931).

New South Wales.

CARNE, J. E. *The Kerosene Shale Deposits of New South Wales.* Mem. Geol. Surv. New South Wales, (1903).

Report of the Newnes Investigation Committee (Sydney, 1934).

South Africa.

WAGNER, PERCY A. Mineral Oil, Solid Bitumens, Natural Gas and Oil Shale. *South African J. of Ind.* **1**, 126–52 (Oct. 1917).

Tasmania.

REID, A. MCINTOSH. *The Oil Shale Resources of Tasmania.* Tasmania Dept. of Mines, Geol. Surv. Mineral Resources no. 8, **1** (1924).

TWELVETREES, W. H. *The Tasmanite Shale Fields of the Mersey District.* Tasmania Dept. of Mines, Geol. Surv. Bulletin no. **11** (1912).

General.

THIESSEN, REINHARDT. *Origin of the Boghead Coals.* U.S. Geol. Surv. Prof. Paper 132-1 (1925).

BLACKBURN, K. B., and TEMPERLEY, B. N. Botryococcus and the Algal Coals. *Trans. Roy. Soc. Edin.*; **58**, III, 841–68 (1936).

SECTION 44

SHALE OILS AND TAR OILS

Scottish Shale Oil	G. H. SMITH, G. GRANT, and S. ALLEN
Estonian Shale Oils	P. N. KOGERMAN
Low-temperature Tar Oils	J. G. KING
High-temperature Coal Tars	W. G. ADAM

SCOTTISH SHALE OIL

By G. H. SMITH, Ph.D., A.I.C., G. GRANT, F.I.C., and S. ALLEN, B.Sc., A.I.C.
Scottish Oils Ltd.

Oil shale as found in the Lothians of Scotland is a dark brown to black, fine-grained solid. It is finely laminated, though frequently this is not apparent until it has been subjected to the action of heat, and, unlike the carbonaceous shale or 'blaes' of the coal measures, it does not disintegrate readily on exposure to the weather. Little is known of the oil-producing substance of oil shale to which the name 'Kerogen' has been given, but undoubtedly it consists of large and complex molecules, soluble to only a slight extent in the ordinary organic solvents, and which break down on heat treatment to form smaller and simpler molecules. Intermediate highly complex molecules are apparently formed during this process, and it is generally recognized that a gradual increase in temperature over the range 350 to 500° C. is necessary in the retorting of oil shale to obtain the maximum yield of oil by allowing the decomposition of the kerogen and of the complex intermediate compounds to take place at as low a temperature as possible.

In the case of Scottish oil shales, decomposition of the organic matter begins at 350° C., the evolution of oil is rapid at 400° C., and at a temperature of approximately 480° C. the evolution of oil is complete. Further increase in temperature results in the further evolution of gas, water, and ammonia, but of no oil.

The analysis of two representative samples of oil shale are given:

	Dunnet Shale Westwood Westlothian	*Camps Shale No. 4 Mine Pumpherston*
	%	%
Hygroscopic moisture	3·25	1·62
Organic hydrogen	2·17	2.10
,, carbon	14·27	13·11
,, nitrogen	0·53	0·53
,, sulphur	0·23	0·25
Carbon dioxide	3·95	9·80
Silica	41·94	34·09
Alumina	17·89	17·54
Iron pyrites	1·02	1·52
Ferric oxide	..	0·80
Ferrous oxide	3·82	3·96
Lime	3·19	9·65
Magnesium oxide	1·49	0·99
Sodium oxide	2·40	0·45
Chlorine (as soluble chlorides)	0·20	0·27
Oxygen and undetermined	3·65	3·32
	100·00	100·00

The yields of products obtained when these samples were heated gradually to 600° C. and maintained at this temperature until the evolution of gas had practically ceased (Gray-King apparatus) are given in the next column.

Retorting of Oil Shale

The two main essentials in the retorting of oil shale are that the material to be distilled be heated gradually over the range of temperature (350 to 500° C.) within which the oil is evolved and that, to avoid unnecessary cracking, the vapours must not come in contact with highly heated surfaces.

Products per ton of shale	*Dunnet Shale Westwood Westlothian*	*Camps Shale No. 4 Mine Pumpherston*
Crude oil	23·5 gal.	21·7 gal.
Gas	1,230 cu. ft.	1,250 cu. ft.
Ammonia as ammonium sulphate	23·2 lb.	27·8 lb.
Spent shale	15·8 cwt.	16·3 cwt.
The total volatile matter consisted of:	%	%
Hygroscopic moisture	3·25	1·82
Crude oil	9·28	8·46
Carbon dioxide (from carbonates)	2·88	3·43
Gas and water (from organic matter by difference)	5·41	4·59
Ammonia (NH_3)	0·28	0·33
Total volatile matter	21·10	18·63

Distribution of Organic Hydrogen, Carbon, and Nitrogen in the above Products

	Dunnet Shale Westwood Westlothian		*Camps Shale No. 4 Mine Pumpherston*	
Organic hydrogen:	%	%	%	%
Oil	1·12	(52)	1·05	(50)
Spent shale	0·32	(15)	0·25	(12)
Gas and water (by diff.)	0·73	(33)	0·78	(38)
Total organic hydrogen	2·17	(100)	2·08	(100)
Organic carbon:				
Oil	7·97	(56)	7·22	(55)
Spent shale	4·88	(34)	4·53	(35)
Gas (by diff.)	1·42	(10)	1·31	(10)
Total organic carbon	14·27	(100)	13·06	(100)
Organic nitrogen:				
Ammonia	0·22	(42)	0·26	(49)
Oil	0·08	(15)	0·06	(11)
Spent shale	0·17	(32)	0·16	(30)
Gas (by diff.)	0·06	(11)	0·05	(10)
Total organic nitrogen	0·53	(100)	0·53	(100)

The retorting of oil shale is therefore very similar to the low-temperature carbonization of coal, and actually a considerable proportion of the retorts proposed within recent years for processing oil shale have been designed primarily for the handling of coal, and repeat ideas tried and discarded many years ago, in the shale industry.

As in all low-temperature processes, the main difficulty in carbonization arises from the fact that oil shale is a poor conductor of heat and that the temperature difference between the retort walls and the material being processed must necessarily be low. In the case of externally heated retorts, the heat transfer will therefore be low and the throughput restricted. This fact, together with the necessity of distributing the heat evenly throughout the mass of shale in the retort, has been responsible for a great multiplicity of retorts of various designs, a summary of which is given below.

Another factor of considerable importance in retorting is the freedom with which certain rich shales soften and swell when heated, tending to agglomerate and adhere to the retort surfaces when processed and so interfering with the free passage of the shale through the retort and escape of the gases. Again, practically all oil shales and the spent shales therefrom form dust by attrition, and this is of major importance, particularly in the case of mechanically operated retorts. The evolution of dust with the oil-vapours, its subsequent deposition in condensers and receivers, and the contamination of crude products resulting in obstinate emulsions is frequently a very serious difficulty.

Classification of Retorting Processes.

(*a*) *Externally Heated Retorts.*

1. Where a carrier is used to convey the heat from the heated retort surfaces to the shale and to distribute evenly the heat throughout the mass to be retorted, the two chief carriers used being steam and the products of the reaction.
2. Where the material to be retorted is by mechanical means stirred to bring it into contact with the heated walls of the retort.
3. Where the material to be retorted is heated in thin layers.

(*b*) *Internally Heated Retorts.*

1. Where the heat necessary for the carbonization process is supplied by the combustion of part or all of the residue containing carbon in the retort, the hot gases so generated passing through the retort in direct contact with the material processed.
2. Where gases of combustion or superheated steam generated outside the retort pass through the retort in direct contact with the material being processed.

Of the externally heated retorts, the type which has attracted the greatest attention during recent years has been the mechanically operated rotary retorts and retorts equipped with mechanical stirring devices. In this case, difficulties arising from the fact that shale is a poor conductor of heat are to a large extent overcome. As a general rule, the material to be processed is either powdered or crushed to pieces of small size before processing, and, by rapidly moving or stirring the shale in contact with the heated walls, a much higher rate of heat transfer can be obtained for a given size of plant than in other forms of externally heated retorts and an even distribution of heat obtained.

The main disadvantage in retorts of this type is the complication of plant associated with this stirring, aggravated by the facts that the moving parts are generally of cast iron or steel and that the mechanical operations are carried out at a fairly high temperature. The shale must be heated to approximately 500° C. to obtain the maximum yield of oil, and normally the heated surfaces are slightly in excess of this. Under these conditions the yield of ammonia is small and no attempt is made to recover this by-product.

Difficulties arising from the evolution of dust are normally considerable, due to the constant stirring of the small material processed, and invariably special plant has to be introduced to deal with the large quantity of fine dust leaving the retort with the oil vapours.

In the case of internally heated retorts, the most important type is that in which the heat necessary for carbonization is supplied by the combustion of the carbon remaining in the spent shale after the oil is evolved. The chief feature of this type is simplicity of design, the retorts being generally vertical, gravity operated, and very similar in essential features to the ordinary coal-gas producer, except that provision must be made for the discharge of much greater quantities of residue.

In the vertical form of retort, air and steam pass into the base of the retort, which is normally the combustion zone, and the gases of combustion and steam pass up the retort in direct contact with the shale. Normally the design allows for a deep layer of shale in the retort so that the rate of increase in temperature of the shale passing down the retort is gradual and the temperature of the vapours leaving the top of the retort, low.

Shales which intumesce in the early stage of heating or which would readily fuse in the combustion zone are difficult to handle in this form of retort, but where suitable shales are processed few operating difficulties are presented. Dust difficulties, in comparison with mechanically stirred retorts, are considerably less, and where the gases and vapours come in contact with shale at low temperatures moist with oil before leaving the retort, they are usually filtered practically free from dust.

The main disadvantage in retorts of this type is the dilution of the hydrocarbon gases from the carbonization process by the gases of combustion resulting in large volumes of gas of low calorific value from which the light spirit is difficult to extract.

Retorting Operations.

While oil shale and torbanite deposits are to be found in many countries, the most intensively developed are those of Scotland, France, Estonia, Australia, and Manchuria.

In the U.S.A. oil shales are of widespread occurrence, but have not yet been commercially developed. Previous to the discovery of petroleum in Pennsylvania there were in existence numerous carbonization plants processing cannel coal. Operations were discontinued with the introduction of the cheaply obtained well oils, but since 1918 a considerable amount of work has been carried out in the surveying and examination of the shales of Colorado, Utah, Wyoming, and California. These operations included large-scale experimental carbonization, using different types of retorts, a summary of which is given by M. J. Gavin [19, 1924].

In Estonia considerable development of the rich 'Kukersite' has been carried out, these operations being described in another section.

In France, while oil shales occur in many places, the only deposit now worked is that at Autun where operations have been continuous for approximately 75 years. The deposits include a proportion of torbanite, and it is stated by Abraham [1, 1920] that, unlike other shales, a proportion of bituminous matter can be extracted from these shales by solvents. The oil content is 8 to 10% by weight, equivalent to 20 to 25 gallons per ton of shale. Retorting operations are carried out in three benches of Pumpherston retorts, the retorts and method of operation being similar to those described later in this section.

In New South Wales [32, 1934] a so-called oil shale exists in considerable quantities. This material, which is more of the nature of a cannel coal or torbanite, gives a high oil yield, the average yield of the shale processed at Newnes in the Wolgan Valley being approximately 100 gallons per ton. Operations have been carried out intermittently since 1905, the main difficulty in processing this rich material being the fact that the shale softens and swells when heated, causing mechanical difficulties in retorting. The report of the Newnes Investigation Committee [32, 1934], which gives an account of these operations, indicates that these difficulties have to a certain extent been overcome by a modified Pumpherston retort (the Fell retort).

Oil shale of Jurassic age is processed at Holzheim, Wurttemberg, in Germany. This shale, which is grey in colour and well laminated, gives a yield of 5 to 6% by weight of oil (equivalent to 11 to 14 gallons per ton). The retort consists of a horizontal externally heated rotating drum 8 ft. in diameter by 72 ft. long fitted with a spiral guide to convey the shale through the retort. The shale is heated to 500° C., at which temperature all the oil is evolved, the average period of carbonization being 2½ hours. In these operations spent shale is one of the main products, being required locally in the manufacture of cement, and to obtain the required quantity, shale is also used as fuel in heating the retort. The throughput of the retort is 90 tons per day, and an equal quantity is used as fuel. The shale is non-fusing, and no difficulty is experienced in obtaining a steady flow of shale through the retort.

At Fushun in Manchuria [29, 1930] large-scale operations have been in progress since the beginning of 1930, processing the oil shale which occurs in large quantities there overlying a valuable seam of coal. The plant, which includes 80 Fushun retorts, is capable of handling 4,000 tons of shale per day. The retort is vertical, gravity operated, and internally heated by gases of combustion and heated permanent gas. It consists of two sections, the upper or distillation zone and the lower or combustion zone, the shale passing down the retort in counter-current to the flow of heating gases. The throughput of the retort is 50 tons per day, the average yield of oil being 5·5% by weight, equivalent to 14 gallons per ton. The average yield of ammonium sulphate is approximately 30 lb. per ton of shale.

In Scotland operations are now confined to the counties of Midlothian and Westlothian, and approximately 1½ million tons of shale are processed per annum. The retorts operating in the Scottish shale-oil industry are based on the principle discovered about 1880 by Young and Beilby that when shale, after being heated to a temperature high enough for the complete evolution of the oil, is heated to a high temperature in a current of steam, the yield of ammonia is greatly increased, and that the maximum yield of ammonia can only be recovered when the combustion of the carbon in the spent shale is complete. Based on this principle, the modern retorts are designed to give the maximum yield of both oil and ammonia, their chief feature being that two definite operations are carried out in the one retort:

(1) The oil is obtained from the shale at a comparatively low temperature in a current of steam in the upper part of the retort, and

(2) After removal of the volatile matter, the combustion of the remaining organic matter in the shale is carried out in the lower part of the retort at as high a temperature as possible and to as complete a stage as possible in an atmosphere of steam.

There are three different designs of retort in operation in Scotland: the Pumpherston retort, the Broxburn retort, and the Young and Fyfe retort. Apart from details of design, however, the three retorts are essentially the same, and there is little to differentiate them so far as yield and quality of the products are concerned. Of the three, the Pumpherston retort, which is described below, is the most efficient mechanically.

In each case the retort is vertical and gravity operated, the shale passing down the retort in counter-current to the flow of steam which, apart from being necessary for the combustion of the remaining organic matter in the lower part, acts as a carrier and distributor of heat. The rate of flow of shale down the retort is controlled by a mechanism at the base of the retort which continuously discharges spent shale into the hopper below.

The Pumpherston Retort.

The Pumpherston retort, patented in 1894, is the most efficient retort operating in the industry. This vertical, gravity-operated retort is circular in section and consists of five essential sections:

(*a*) The charging hopper, holding 4 tons, i.e. a day's supply of shale.

(*b*) The cast-iron part of the retort, 11 ft. 6 in. high, 2 ft. dia. at the top, and 2 ft. 4 in. at the bottom. The vapour off-take is situated at the top of this section.

(*c*) The firebrick part of the retort, approximately 20 ft. high, is 2 ft. 4 in. dia. at the top where it joins the metal section, and 2 ft. 9 in. at the bottom.

(*d*) The discharge mechanism. The charge of shale rests on a cast-iron table at the bottom of the firebrick section of the retort. On this table a curved arm slowly rotates, pushing the spent shale over the edge into the spent-shale hopper below.

The retort is heated externally by the scrubbed permanent gas from the retorting operations augmented by a small proportion of producer gas, the gas entering the heating flues at the bottom of the firebrick section and by a system of baffles being made to take a path upwards and around the retort to ensure even heating. The external temperature near the bottom of the retort is maintained at approximately 1,000° C. with a gradual reduction to about 550 to 600° C. in the metal zone.

Low-pressure steam, usually the exhaust from the power plant, is admitted (at the bottom of the retort), cooling the spent shale before discharge and passing superheated up the retort. The quantity used is approximately 1,000 lb. per ton of shale, and as the specific heat of steam is twice that of shale, the steam obviously plays a very important part as a carrier of heat in the retort.

The daily throughput of shale per retort is 4 tons, and in passing down the retort it is gradually heated to a maximum temperature of 650 to 700° C. The oil is evolved over the range 350 to 480° C. in the upper part of the retort, and at the higher temperatures existing in the lower part, the remaining carbon is converted into water-gas and the nitrogen evolved as ammonia. The capacity of the heated section of the retort is 4 tons, and the average time taken for the shale to pass through this section of the retort is 24 hours. Lump shale is normally processed, the shale from the mines being coarsely broken to give a maximum size of half a brick with varying sizes downwards and with the minimum of 'smalls' or 'fines', as these would interfere with the free passage of the steam and vapours through the retort.

The products of retorting shale are oil, ammonia water, and gas. The gas, however, contains appreciable quantities of ammonia and spirit, and these are extracted from the gas by scrubbing with water and oil respectively. The spirit-recovery plant is of conventional oil-absorption design, except that instead of bubble-cap trays the absorption towers are packed with wood in such a manner as to reduce to a minimum the possibility of choking by dust from the retorts. The equipment for denuding the gas oil of spirit is of the usual steam-stripper type. As the upper portion of the retorts, and the mains, condensers, &c., are all under suction, the gas contains a considerable proportion of air, so that the analysis of unscrubbed gas given below has been calculated to an air-free basis:

Analysis of Gas

Nitrogen	14·3
Carbon monoxide	6·1
Carbon dioxide	31·4
Hydrogen	38·2
Methane	9·06
Ethylene and ethane	0·36
Propylene and propane	0·22
Butylene and butane	0·16
C_5	0·08
C_6	0·06
C_7	0·03
C_7 + higher	0·03
	100·00

Spent Shale.

Spent shale from retorting operations may amount to as high as 80% by weight of the shale processed, and its disposal, necessitating haulage charges and the cost of ground, involves additional expense. In Scotland, until recently, the only useful purpose which these 'bings' of shale served was the filtration of works effluent. It has been shown, however, that first-class bricks can be produced from Scottish spent shale, and large-scale production of building bricks is now carried out at Pumpherston, Midlothian. These bricks are produced by methods resembling in some respects those employed in the sand-lime process.

Spent shale can also be used for the production of cement, and at Holzheim, Germany, spent shale is one of the main products of the carbonization operations, the whole of the output being used for this purpose.

Chemical Composition of Shale Oil

Shale oil is the product of thermal decomposition of the organic matter 'kerogen' in oil shale. This kerogen has not, so far, been isolated. Attempts to extract this material with the various solvents, petroleum ether, benzene, carbon disulphide, chloroform, acetone, alcohol, phenol, aniline, and pyridine, have met with only partial success. Good results were reported by Gavin and Adyelotte [21, 1922], who extracted by organic solvents up to 10·98% of certain shales, or 55·8% of the distillation yield of oil. Hentze [26, 1922] attacked the shale Kukersite with hydrochloric acid followed by hydrofluoric acid, and then extracted the residue with chloroform, but only succeeded in isolating 72% of the bitumen in the shale.

McKee and Goodwin [30, 1923] and Blackburn [7, 1924] by distillation of shale under reduced pressure obtained an 'intermediate product' between the kerogen and shale oil. The former showed the intermediate product to be highly unsaturated, that from Californian shale being completely soluble in sulphuric acid (sp. gr. 1·84), while that from Colorado shale showed 11% saturated hydrocarbons (insoluble in H_2SO_4). Subsequent distillations of these primary products gave respectively 52 and 38% insoluble in sulphuric acid (sp. gr. 1·84).

Botkin [9, 1921] determined the effect of distillation on the saturated hydrocarbon content of shale oils of three types—asphaltic, paraffinic, and mixed base oil—and in each case the distillates were more saturated than the original oils, this decomposition being accompanied by the formation of gas and coke. Successive distillations had, however, very little effect on the percentage of saturated hydrocarbons.

The evidence leads to the conclusion that the highly unsaturated product from the primary decomposition of the 'kerogen' is further decomposed by heat to yield more saturated oils, gas, and coke, and that the nature of the shale oil is affected by the extent to which this process takes place during the retorting of the shale. The quality of a shale oil, therefore, depends on the nature of the oil shale, the design of the retort, and the temperature and rate of retorting.

Shale oils are considered to consist chiefly of paraffins, olefines, and naphthenic hydrocarbons, together with varying proportions of sulphur, nitrogen, and phenolic compounds. Aromatic hydrocarbons are, according to Hellsing [24, 1921], present in Swedish shale oil. Several investigators have reported the presence of aromatics in the lighter fractions of Scottish shale oil, but this is not in accordance with Bailey's [3, 1927] findings, and recent work on this subject confirms Bailey's view that aromatics are not present to any appreciable extent in at least the spirit fraction of Scottish shale oil.

As regards the individual hydrocarbons present in shale oil, little is known of the heavier fractions, but some work has been reported on the composition of the lighter fractions, and below are given two analyses of refined spirit derived from retort gases when treating Scottish shale.

	Garner [17, 1928]	*Author* [1935]
Paraffins	43·5	42·5
Naphthenes	9	9·5
Unsaturated hydrocarbons	39	48
Aromatics	8·5	nil

B. Steuart [35, 1900] isolated from Scottish shale oil the paraffins, normal and isopentane, heptanes and hexanes, and possibly the naphthenes, methyltetramethylene, pentamethylene, hexamethylene, and methylhexamethylene, and reported the presence of aromatics. Hellsing [24, 1921] identified the aromatics, benzene, toluene, *m*-xylene, and cumene in Swedish shale oil, and later Holmberg [28, 1928] confirmed this when he identified benzene, toluene, and xylene in the light fractions of a shale oil from a similar source.

Diolefines and acetylene derivatives are also present to a small extent in shale oil.

McKinney [31, 1924] from an acetone extract of New Brunswick shale isolated 28 hydrocarbons of the paraffin, naphthene, and hydro-naphthalene series.

Sulphur. The sulphur content of shale oils varies greatly according to the nature of the oil shale from which it is produced. Scotch shale oil contains 0·4%, Kimmeridge shale oil has 4–8%, while the Ichthyol shale oils have as much as 3–10% sulphur. No economical method has, so far, been worked out to refine these high sulphur Kimmeridge shale oils, but Ichthyol is produced from the Tyrolese and similar shale oils.

Franks [15, 1921] determined the sulphur content and its distribution in distillates from Colorado shale oil, and showed that the very light oils contain the least sulphur, the 20–30% cut the greatest, while the cracking which takes place towards the end of the distillation results in a loss of 29·3% of the total sulphur content.

In the case of Scottish shale oil the lightest fractions contain least and the heavier fractions most sulphur. For example, on distilling a shale oil of sulphur content 0·41%, the first 10% contained 0·18% sulphur, and each successive 10% fraction showed a corresponding increase in sulphur, leaving a 17% residue containing 0·42% sulphur. The loss of sulphur through decomposition amounted to 20%.

The sulphur compounds of the light fractions from Scotch shale oil are principally sulphuretted hydrogen, mercaptans, thio-ethers, and thiophens. Carbon disulphide is absent.

Challenger [10, 1926] made a comprehensive study of Kimmeridge shale oil, and isolated and identified the following compounds: thiophen, 2-methylthiophen, 2:3-dimethylthiophen, 2-ethylthiophen, tetrahydrothiophen, and possibly thionaphthene.

Nitrogen. Nitrogen is present in Scottish shale oil to the extent of 0·6 to 1·0%, depending on the shale and the retorting conditions. Beilby [6, 1891] showed that approximately one-fifth to one-quarter of the total nitrogen present in the shale appears in the oil, but on distillation to coke a large proportion of this nitrogen is eliminated during the cracking which takes place at the latter end of the distillation. Bailey [5, 1927] found that the loss on treatment of four Scottish shale oils with sulphuric acid, 10% strength, varied from 12 to 18%, but this loss cannot be taken as due entirely to nitrogen bases.

As regards the actual nitrogen compounds present in Scottish shale oil, Robinson [33, 1879] and Robinson and Goodwin [34, 1880] identified the following bases of the leucoline series: $C_{12}H_{13}N$, $C_{13}H_{15}N$, $C_{14}H_{17}N$, $C_{16}H_{21}N$; while Garret and Smythe [18, 1902–3] isolated and identified from the fraction boiling below 164° C. pyridine, 2-methyl pyridine, 2:6-dimethyl pyridine, 2:4-dimethyl pyridine, 2:5-dimethyl pyridine, 2:4:6-trimethyl pyridine, and from the fraction above 164° C. 2:3-dimethyl pyridine and 2:4:6-trimethyl pyridine.

The distribution of nitrogen in three samples of Colorado shale oil was investigated by Franks [16, 1921], who found these oils to contain from 1·5 to 1·85% nitrogen and that the heavier fractions contained by far the largest amounts of nitrogen.

Phenols. Scottish shale oil has a phenol content of from 2 to 4%. In the crude naphtha fraction of this oil Gray [23, 1902] detected and separated phenol, *o*-cresol, *m*-cresol, xylenols, and showed the presence of guaiacol. The crude spirit from cracking Scottish shale oils contains about 1% of phenols, from which the following have been isolated: cresols, xylenols, and higher phenols, xylenols predominating. Guaiacol could not be detected.

Refining of Shale Oil

The problem of producing marketable products from shale oil is complicated by the presence of nitrogen bases, phenolic bodies, unstable unsaturated compounds, and in some shale oils, such as those from the Kimmeridge shales, excessive quantities of sulphur compounds. These bodies are responsible for the discoloration, unpleasant smell, and gumming tendencies which are found in crude shale-oil distillates.

Distillation and treatment with sulphuric acid and caustic soda solution are still the fundamental basis of refining shale oil, and although the very high acid treatments with consequent high losses of former days have been reduced to a minimum, the average shale oil only yields about 80% by volume of finished products.

In any refining scheme where motor spirit is the principal product desired, cracking or destructive hydrogenation is essential.

A method of refining which provides the greatest possibility of eliminating the now unavoidable loss is destructive hydrogenation, but while the technique of this process has been more or less thoroughly worked out, the costs are still considered to be too high to permit of practical application. That this process offers scope for improving yields can be realized when it is considered that present-day methods of refining shale oil have as their object the removal, as far as is essential, of nitrogen bases, phenolic and sulphur compounds, and unstable diolefines, while hydrogenation simply replaces with hydrogen the elements nitrogen, oxygen, and sulphur, producing ammonia, water, and hydrogen sulphide which can easily be eliminated; the diolefines are saturated so that yields of close on 100% by volume can be reasonably expected. Another valuable feature of hydrogenation is that by varying conditions the process can be adapted to yield products ranging from motor spirit to fuel oil.

The refining of shale oil in France is effected in much the same manner as in Scotland, i.e. by distillation and treatment with sulphuric acid and caustic soda. Minor differences in operation exist, but in principle both methods are similar. Colorado shale oil derived from experimental retorting runs was refined by George [22, 1921], and while many refining agents were explored, it was concluded that distillation, sulphuric acid, and caustic soda gave the most satisfactory results. Data on the refining of oil from Ermelo torbanite in the Union of South Africa have been recorded by Bleloch [8, 1931], but here again sulphuric acid and caustic soda were the agents employed.

The Newnes Investigation Committee [32, 1934] considered various methods of refining cracked spirit from Australian shale oil, and concluded that for the preparation of a finished spirit conforming to Australian standards, there was no alternative to the orthodox method of treating with sulphuric acid and caustic soda.

Attempts to deal with the high sulphur Kimmeridge shale oil have so far met with little success.

The chemistry and refining of Estonian shale oil is dealt with in another contribution to the technology of oil shale.

Refining of Scottish Shale Oil.

In past years the refining of Scottish shale oil has been described in detail by various writers, principally by Steuart [36, 1912], Gavin [20, 1924], and Bailey [4, 1927]. The last-named author describes the refining operations as carried out in 1927 in great detail, and his paper constitutes a notable contribution to the technology of the shale-oil industry. Much of the refining equipment therein described is in commission to-day.

To illustrate the various methods of refining to meet specific demands, the following schemes of operation are briefly described:

1. Full refining, i.e. production of motor spirit, kerosine, gas oil, lubricating oil, wax, and fuel oil.
2. Production of the maximum quantities of motor spirit, i.e. complete cracking programme.
3. Manufacture of maximum amount of Diesel oil.
4. Combination of any of above schemes.

All these processes, except the full cracking process, which is dealt with later, have the same preliminary operations in common, including the fundamental features of distillation, acid and soda treatment, and wax extraction. The full refining process is shown diagrammatically on page 3103, and as (3) and (4) are variations of (1), this diagram will serve to illustrate the preliminary steps of all. The diagram is that given by Bailey, but altered to incorporate later developments.

The oil products from retorting shale are (1) crude spirit recovered from the gas evolved in the process, and (2) crude oil collected from the condensing equipment. In Scottish practice these two products are refined separately.

The crude spirit from the gas contains 90–3% distilling to 175° C., and together with the naphtha from the crude oil is refined with sulphuric acid (sp. gr. 1·84) and caustic soda, followed by redistillation and plumbite treatment. The refined spirit amounts to about 90% of the crude spirit and has a final boiling-point of 180–185° C., volatility at 100° C. of 35%, and octane number of 58 C.F.R. (motor). From the heavy portion of the crude spirit various solvent naphthas are prepared. These naphthas, by virtue of their comparatively high unsaturated hydrocarbon content, are excellent solvents and are largely used in the rubber, linoleum, paint, and cleaning industries.

An analysis of a sample of crude shale oil is given below:

Sp. gr. at 60° F.	0·878
Initial boiling-point	164° C.
Dist. to 150° C.	..
„ 175° C.	1·0%
„ 200° C.	4·0%
„ 225° C.	10·0%
„ 250° C.	17·5%
„ 275° C.	24·5%
„ 300° C.	34·5%
Sp. gr. of dist. to 300° C.	0·824
Residue above 300° C.	64·5%
Sp. gr. of residue	0·908
Ultimate Analysis:	
Carbon	85·83%
Hydrogen	12·64%
Nitrogen	0·74%
Sulphur	0·46%
Oxygen (diff.)	0·33%

The full refining of the crude oil may be conveniently described under the following sections:

(1) First distillation, acid and soda treatment, second distillation.
(2) Kerosine and gas-oil production.
(3) Wax extraction and refining.
(4) Lubricating-oil production.

First Distillation, Acid and Soda Treatment, Second Distillation.

Crude shale oil is first subjected to a distillation to coke, whereby the most unstable compounds of high boiling range are decomposed into more saturated hydrocarbons, coke and gas, so that besides effecting a first separation of the liquid products, this distillation constitutes a first refining step. The distillation is carried out in a battery of five boiler stills running continuously and in series with twenty-eight coking stills which are operated batchwise.

The products of this first distillation are (1) crude naphtha, (2) crude distillate, (3) shale resin, (4) coke. The first three amount to 96–7% of the total charge, while the coke accounts for 1·5%; the remainder is gas. The naphtha is removed and refined with the recovered spirit from the retort gases. The coke on account of its purity is a valuable product, and is used principally for making carbon electrodes for the aluminium industry.

The crude distillate consists of the combination of all liquid products with the exception of crude naphtha. This blending of these distillates is necessary, so that the oil is of sufficient fluidity to permit of acid and soda treatment at reasonable temperature. If the heavier fractions were refined separately, then to get a mobile oil and a fluid tar the oil would have to be heated to such a high temperature that the losses on acid treatment would be prohibitive.

The acid and soda treatment of the crude distillate may be carried out in any conventional type of washer at a temperature of about 50° C. The losses incurred during treatment are heavy. The treated oil is next separated into its components, crude burning oil, heavy oil and paraffin, and coke, by a second distillation in a battery of boiler stills and 'pot' stills exactly similar to those employed in the first distillation. Steam, however, is cut off the coking stills during the latter part of the distillation, so that asphaltic bodies which would hinder the crystallization of paraffin wax are cracked, thereby rendering the subsequent purification of wax much simpler. The loss in this distillation is again of the order 1–2%, but the coke, since it contains a small proportion of soda, is unsuitable for industries where a pure product is required, but is an excellent household fuel.

Kerosine and Gas Oil.

The crude kerosine cut from the second distillation is treated with sulphuric acid (sp. gr. 1·84) and caustic soda solution and distilled with steam; the fractions taken off as distillates constitute the various grades of kerosine from power oil to the heaviest lighthouse grade. Continuing the distillation beyond the kerosine range, light gas oil is obtained. The losses on the acid and soda treatments are very heavy, and many alternative methods of refining have been examined both in the laboratory and on works tests, to cut down this loss and at the same time to produce a more saturated oil and one of lower sulphur content.

Refining by adsorbent earths, either natural or highly activated, or combined with acid and soda treatment, give a slightly better burning oil than the straight acid and soda process, but the comparatively large quantity of material necessary to give any appreciable improvement offsets the advantages to be derived. In the case of bauxite, which is one of the best earths for this purpose, 3 to 4 lb. per gallon are required, together with a previous light acid and soda wash.

An excellent kerosine of low sulphur content can be prepared by extraction of the undesirable constituents from the burning-oil fraction by liquid sulphur dioxide. The method of operation is essentially that employed for petroleum kerosines with the addition of a final distillation. In brief the process consists of separating the kerosine fraction from the crude, washing with caustic soda to remove hydrogen sulphide, drying, treating with liquid SO_2 at 10 to 14° F., washing the refined oil with acid and soda, and finally distilling the product, taking off 95% as kerosine. This final distillation is necessary, as without it the product contains constituents which cause excessive char formation on the lamp wick and consequently gives a bad burning test. The characteristic smell of shale oil is entirely absent from this product. The SO_2 extraction divides the kerosine into 70% refined oil and 30% extract, but unfortunately the extract is not of value as an anti-knock agent as in the case of the SO_2 extract from most petroleum kerosines. The light fraction of distillation range 137 to 210° C. has an octane number of approximately 60 C.F.R., which is too low to be of use as a blending material, nor is the heavier fraction of the extract of appreciable service in augmenting the knock rating of vaporizing oils. The SO_2 extract has, therefore, little more than fuel-oil value, which renders this process very costly.

By virtue of its comparatively high unsaturated hydrocarbon content, shale power oil has a definite advantage over the corresponding fractions from paraffinic or mixed base petroleums in that it has a fairly high anti-knock value and at the same time is a serviceable burning oil, a combination which is much appreciated where, as in fishing fleets, the same oil is used for both power and light.

Extraction and Refining of Paraffin Wax.

The heavy oil and paraffin fraction from the second distillation amounts to 50–60% of the crude oil. It has a specific gravity of 0·864, a setting-point of 80° F., and a viscosity (Redwood no. 1) of 35 sec. at 140° F. This fraction is very suitable for satisfactory processing, and is cooled in refrigerating plant by direct expansion of liquid ammonia. The paraffin wax crystallizes out from the oil, and the pasty mass is then pumped into filter presses at high pressure, so that a crude wax or 'scale' is obtained as free from oil as possible, the expressed oil being termed 'Blue Oil'. Extraction of the scale in two stages is both convenient and necessary when many grades of wax are required. The first stage of cooling is to 32° F., yielding a crude hard wax; the expressed oil is then recooled to 15–20° F. and filter pressed, giving a soft scale which can be refined into good-quality wax of low melting-point. The total scale constitutes about 20% of the heavy oil and paraffin.

The refining of the crude wax must be conducted with great care if refined wax of the highest quality is to be obtained. The 'sweating' plant at present in use is the tray-type stove, designed by N. M. Henderson [25, 1891]. The process is carried out in sweating houses or ovens, which are brick buildings containing sets of large pans or trays with the necessary connexions, with steam pipes for heating, according to the well-known general arrangement of this plant. The melted crude wax is pumped on to the trays, which are partly filled with hot water, and allowed to solidify. The water is then run off and the house closed. The temperature is slowly raised, to allow the oil and low melting-point waxes to drain away. When the required quality of wax is left on the trays it is then melted by steam and run into receivers, ready for the decolorizing process.

The quality of the crude paraffin scale is most important and must be carefully controlled. It should be of pale colour, and should not contain more than about 12% of oil, otherwise it is more difficult to obtain a good coloured sweated wax and excessive strainings have to be disposed of. The scale must also be of needle-shaped crystalline structure, and to produce this the crude hard scale (m.p. 116° F.) is mixed, before sweating, with enough crude soft wax or strainings from previous operations to reduce the melting-point to about 107° F. From this mixture are prepared grades of refined wax of m.p. 130–135° F., 125–130° F., 122–125° F., 118–120° F., and 115–118° F. The soft scale (m.p. 90° F.) is used for the manufacture of grades of m.p. 110–115° F., 106–108° F., and 98–102° F. Both hard and soft scales produce wax of excellent quality when fully refined.

The sweated wax, however, has to be decolorized to produce wax of high-grade marketable quality. This is accomplished by slow filtration of the molten sweated wax through a tall vertical column of granulated fuller's earth, 16–30-mesh grade, previously activated by ignition in a rotary furnace. Scottish shale wax has been successfully treated with prussiate charcoal, special wood-charcoals, and certain clays in a very finely divided condition, intimately agitated with the molten wax, settled, and filtered, but the best results have been obtained with fuller's earth from the U.S.A. which, in various ways, is more satisfactory and reliable than bauxite.

After filtration of the wax the filters are allowed to drain for some hours. Naphtha is then circulated to dissolve the wax still adhering to the filtering medium; this is recovered by distilling off the naphtha with steam, the solvent being condensed and used repeatedly. The fuller's earth is freed from naphtha by steaming, and is then discharged from the filters and reactivated in a rotary furnace for further use. The loss amounts to about 4%, only the mechanical loss as dust having to be compensated for by the introduction of fresh material.

The decolorized wax is cast into cakes for candle manufacture or for supplying the home and export market. The molten wax may either be run into air-cooled trays or into water-cooled moulds, the latter method being quicker and yielding cakes which are more opaque and smoother on the surface than those obtained by air-cooling.

With regard to the composition of Scotch shale paraffin wax, Francis [14, 1922; 13, 1924] found that, in wax melting between 55 and 56° C., about 80% was composed of seven hydrocarbons of constant boiling-point. Of the remainder, 8 to 10% was composed of material boiling between 220 and 240° C., and the amount of wax boiling above 240° C. (pressure 0·05 mm.) probably did not amount to more than 2 or 3%.

Lubricating Oils.

The lubricating oils obtained from Scottish shale oil are of comparatively low viscosity, 55–60 sec. Redwood no. 1 at 140° F., and are used mainly for batching, blending, and as spindle oils. The dewaxed blue oil is treated with sulphuric acid (sp. gr. 1·84) and caustic soda solution, and the lubricating-oil fractions are separated from the treated blue oil by distillation in a bench of boiler and coking stills similar to those used in the first and second distillations; in this case, however, it is found advantageous to add a small quantity of caustic soda to each coking still at the beginning of the distillation. The products of this distillation are: (1) gas oils, (2) lubricating oils, and (3) coke. The lubricating-oil cuts are dewaxed to the desired setting-point, and were formerly finished by treatment with sulphuric acid (sp. gr. 1·84) and neutralized by sodium carbonate solution. This method resulted in very high losses, trouble with emulsions was frequently experienced, and the finished oils on prolonged storage were liable to go off colour. The acid and soda process gave way to acid and bleaching earth. The unfinished oil in this case is treated with the same quantity of acid and then with bleaching earth, together with a small quantity, usually about 1%, of soda ash at 212° F. Treatment is best effected by pump agitation circulating at high velocity through a steam heater of tube and shell type. The solid material is filtered off at the maximum temperature of the process and at a pressure of 200–50 lb. per sq. in. The filtered oil is cooled, but on standing overnight cloudiness develops and the oil has to be filtered cold before transferring to stock. Many types of filter-cloth have been tried to dispense with this second filtration, but without success. One point of difference between processing this oil and the corresponding petroleum oil is that lime cannot be used as the neutralizing agent, as this yields a much darker and less stable product. As compared with the acid-soda ash process, the acid-clay process yields a better coloured product of greater stability and with a lower refining loss.

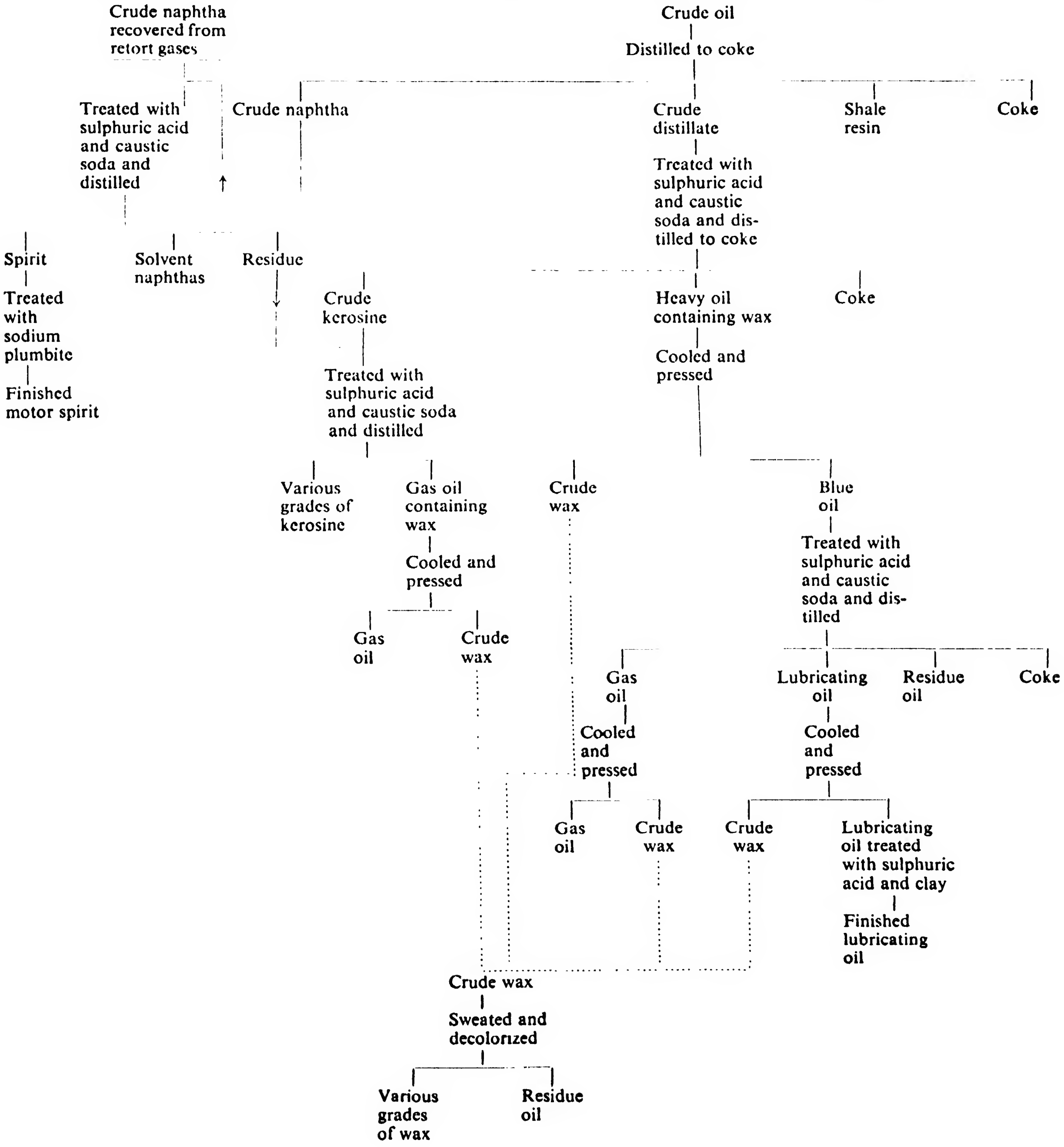
The action of many bleaching earths and clays, both activated and in their natural state, contacted at various temperatures, both by agitation and filtration, has been examined, and almost invariably the highly activated earths have been the most successful and the bleaching action of these materials most effective on acid-treated oils; even such low acid treatments as 0·1% increased the efficiency of the earth enormously. The loss on clay treatment is directly proportional to the quantity used, so that generally the most active earth is the most economical even though it be more expensive. The cost of the best highly activated bleaching earths is so high that many attempts have been made to reactivate them, but none of the processes worked out has been wholly satisfactory.

The refining of Scottish shale oil, as described above, aims at producing the full range of products from motor spirit to coke. The various operations involved in this method of refining are shown diagrammatically below.

Alternative Methods of Refining.

The full refining scheme just described can be modified within wide limits to produce those products which are in greatest demand, and to illustrate the possible variations a few cases are considered below:

(1) Should the maximum quantity of spirit be desired, all the crude oil (not including scrubber naphtha) would



be cracked and, as shown under the section on Cracking, Scottish crude shale oil yields 50 to 60% spirit, together with a heavy furnace oil, gas, and coke.

(2) If wax as well as motor spirit is required, then the crude oil would first be distilled, the wax cut isolated, and the crude wax extracted, the remainder of the crude oil being cracked. Under these conditions, however, the wax is more difficult to refine and requires a treatment with sulphuric acid (sp. gr. 1·84), followed by washing with soda ash and water. It is important to note that the final water wash must be efficient as, if any soda ash be left in the wax, the subsequent sweating is rendered more difficult.

(3) To produce the maximum quantity of kerosine and wax, together with motor spirit, then the full refining scheme would be followed to the point where blue oil is obtained. The blue oil and light gas oil would then be combined and fed to the cracking plant.

(4) Refined shale-oil distillates of suitable distillation range are good fuels for the compression-ignition engine, but care must be taken to ensure that these distillates have been satisfactorily dewaxed; this applies particularly to fuels for high-speed engines. Blue oil can either be blended with light gas oil, or each of these can be used alone for this purpose, depending on the grade of oil specified.

Cracking Shale Oils

Although some information is published on the yields and quality of products obtainable by cracking shale oils, most of it refers to experimental work, but in Scotland shale-oil cracking has been carried out extensively during the past 6 years.

Egloff [11, 1928] records the results of his work on cracking shale oils from different sources—U.S.A. (Green River and Utah), Canada (New Brunswick), France (Autun), Australia, and Scotland. Generally this author gives yields when cracking to both coke and to a residuum fuel oil. The yields given for the shale oils studied, however, are not strictly comparable, as the temperature and pressure of cracking varied between 414 and 449° C. and 120 and 175 lb. per sq. in. respectively.

Cracking to a residuum oil the shale oils detailed above gave yields of spirit F.B.P. 225° C. varying from 35·2 to 55·3%, depending on the nature of the oil, cracking conditions, and quality of residuum oil. This author also completed a series of tests on Green River, Utah, Canadian, and Scottish shale oils, cracking to coke. Under these conditions the yields of refined spirit F.B.P. 225° C. recorded, ranged from 52·1 to 59·6%. Egloff, working on Californian shale oil at lower temperature and pressure, 404° C. and 80 lb. per sq. in., only realized a yield of 40% of refined spirit of the same F.B.P.

Later, Egloff and Nelson [12, 1932] investigated the cracking of Manchurian shale oil, but at much higher temperatures and pressures. Again, operations both to residuum and to coke were investigated and the following yields obtained:

	Residuum oil	*Non-residuum*
Pressure, lb. per sq. in.	350	300
Temperature	930–50° F.	935° F.
Yields: Refined spirit	53–6%	67·5%
Fuel oil	33–26%	. .

The Newnes Investigation Committee [32, 1934] dealt with the cracking of Australian shale oil and concluded from the information submitted to them that this oil could be cracked satisfactorily. Calculations based on figures in their Report indicate that when cracking to residue fuel oil of U.S. Bunker C. grade yields of 48% spirit and 36% of fuel oil could be realized; when cracking to viscosity breaking only 25% of spirit together with 15% of kerosine and 47% of fuel oil could be obtained.

Cracking of Scottish Shale Oil.

Cracking of shale oil as practised in Scotland is in principle a liquid-phase process. Crude oil and blue oil (dewaxed heavy oil and paraffin) can both be handled in these units without difficulty, giving 50–60% of spirit and 30–20% of heavy fuel oil.

This low-temperature liquid-phase operation gives a maximum yield of spirit, but the spirit is of comparatively low octane number. Spirit of higher octane rating can be produced from the gas-oil and kerosine cuts by operating at a higher temperature either in a vapour-phase or high-pressure plant. Spirit production, however, under these conditions is much reduced.

While no individual fractions of Scottish shale oil, apart from blue oil, have been processed in these commercial units, various fractions including blue oil have been subjected to similar cracking treatment in a laboratory autoclave. The yields given below, while they do not apply to plant operations, are strictly comparable and indicate the comparative value of the cracking stocks. Cracking in all cases was carried out to gas and coke. The spirit yields refer to unrefined spirit of F.B.P. 200° C.

Cracking stock	*Yield of cracked spirit, % by volume*
Crude shale oil	62·0
Crude shale-oil distillate	63·0
Acid and soda treated crude shale-oil distillate	65·7
Blue oil	65·0
H.O. and paraffin	68·4
Paraffin wax	78·9
Kerosine	83·1

The heavy furnace oil produced in the cracking operations referred to above is practically solid when cold, but can be pumped hot through insulated lines to various parts of the refinery for use as fuel. Further distillation of this material yields a small proportion of cracking-plant recycle oil and pitch. Softening-point and penetration of this pitch are naturally dependent on the extent of this distillation, and can be further controlled by air-blowing. By this combination pitches of softening-point up to 300° F. are prepared for special purposes. Shale pitch of softening-point 160–170° F. is largely used as a binding agent in briquetting coal, while other grades can be used for road-making, or, when combined with spent shale or other filler, yield artificial rock asphalts.

Refining of Cracked Spirit.

Compared with the spirit recovered from retort gases, this cracked spirit contains more sulphur, phenolic bodies, and pyridine bases, and is of lower octane number.

It is interesting to note that the spirit obtained by cracking shale oil at low temperatures and pressures is a more saturated spirit than that recovered from the retort gases, and this increase in proportion of saturated compounds probably accounts for its comparatively low octane rating. Below are given the approximate composition of shale cracked spirit and the spirit recovered from retort gases:

	Shale cracked spirit, % by volume	*Spirit recovered from retort gases, % by volume*
Paraffinic hydrocarbons	56·0	42·5
Unsaturated hydrocarbons	32·0	48·0
Naphthenic hydrocarbons	12·0	9·5
Aromatic hydrocarbons	nil	nil

The absence of aromatic hydrocarbons from either spirit is noteworthy.

The most satisfactory refining agents are, once more, caustic soda and sulphuric acid, which are employed in conjunction with redistillation and a sweetening treatment. The initial refining process consists of subjecting the crude spirit to caustic soda solution, followed by acid tar, sulphuric acid (sp. gr. 1·84), and finally caustic soda solution. These operations are carried out in a pump-orifice washery. The distillation of the spirit so treated is effected in a pipe-still bubble-tower unit. Sulphur dioxide is evolved during the last operation, particularly if the temperatures reigning are excessive, and since this gas not only rapidly attacks the condensing and run-down equipment, but adversely affects the subsequent plumbite treatment, it is removed by injecting a weak caustic soda solution into the spirit-vapour stream immediately before entering the condensers. The final sweetening with plumbite consists essentially of two stages: (1) plumbite treatment, (2) water washing, for both of which a pump washery is utilized, but in (1) the arrangements are such that the plumbite is regenerated *in situ*.

The refining of cracked spirit from shale oil according to the above scheme necessitates very careful control; insufficient refining results in a product of bad and/or unstable colour and disagreeable smell.

The function of the acid treatment is principally to remove pyridine base compounds and polymerize or eliminate gum-forming bodies such as diolefines. Too little acid yields an unstable spirit, having the faint, unpleasant odour peculiar to pyridine compounds, which is not destroyed by the subsequent sweetening process; such a product is usually slightly off colour, and on storage reverts rapidly in colour. On the other hand, too heavy an acid treatment is undesirable, since in such circumstances larger volumes of SO_2 are evolved during the distillation, with the adverse results indicated previously; in addition, the pressure distillate bottoms are black, containing free carbon, and are strongly acidic, which renders them unsatisfactory for further cracking.

The success of the plumbite treatment is, among other factors, dependent on the efficiency of previous caustic soda treatment. Crude cracked spirits, particularly those derived from cracking crude oil, have a comparatively high phenol content (up to 1%), and should the caustic soda treatment be inadequate, a portion of these acidic bodies comes forward in the rerun spirit to the plumbite plant. The result of this is twofold.

(1) In the particular plumbite process employed the same plumbite solution is used repeatedly, and if the phenol content of the cracked spirit is high, the strength of the caustic soda solution decreases rapidly, lead combines with the phenols in the spirit and ultimately passes into the spirit phase. In especially bad cases this state is at once obvious, as the spirit is of bad colour, and when exposed to light deposits a heavy precipitate, but it is possible to get a clear water-white spirit apparently satisfactory, which, on being subjected to light and/or heat for a considerable time, becomes turbid and ultimately throws down a slight precipitate. Investigation has shown that in all such cases, if the spirit be washed thoroughly with water, these phenol-lead compounds are removed as a sludge, leaving a colour-stable water-white spirit. For this reason a final water wash is an essential part in plumbite treating cracked shale spirits. As well as the adverse effect of processing a spirit of high phenol content outlined above, it need scarcely be stated that the lead consumption under these conditions is excessive.

(2) When plumbite treating a spirit containing phenols in a plant where repeated circulation of plumbite is practised, phenols are extracted by the caustic soda and oxidized by air (either dissolved in the spirit or drawn in during the process) to highly coloured bodies, which, as the plumbite is repeatedly used, increase in concentration until finally the colouring matter redissolves in the spirit. This colouring matter is distinct from that discussed in (1), in that a spirit so coloured does not contain lead, nor is the colouring matter removed by washing with water. This type of colour formation is accelerated by increase in temperature and by prolonged plumbite treatment, so that, to a certain extent, this formation of colour can be minimized by maintaining the temperature and time of the treatment as low as possible, but it can only be eliminated by the complete removal of phenols from the spirit in the preliminary caustic soda wash.

To sum up, experience has shown that the refining scheme given above for shale cracked spirits is satisfactory and economical, provided that the following points are observed: (1) adequate caustic soda treatment, (2) sufficient but not excessive acid treatment, (3) low temperature of distillation, (4) minimum temperature and time of plumbite treatment, (5) efficient water washing.

Refinery Gases and Tars.

Compared with petroleum refining, the losses incurred in producing marketable products from shale oil are high (this does not apply to cracking) and are principally due to the formation of tars when treating the oil with chemicals and loss as gas (in distillation, particularly coking distillations).

Both cracking gases and gases from the distillation units contain spirit (see analyses below), and in Scottish practice these gases are all collected and the spirit recovered by the conventional gas-oil absorption process. The dry gas is used as fuel.

Analyses of gases	*Cracking gas*	*Gas from distillation units*
	%	%
Air and nitrogen	1·5	10·0
Carbon monoxide	1·5	1·0
Hydrogen	3·9	7·6
Methane	49·1	51·0
Ethylene	1·2	1·4
Ethane	27·78	9·6
Propylene	2·77	2·6
Propane	11·28	5·5
Butylenes	1·55	2·2
Butanes	4·00	1·8
C_5	1·85	3·3
C_6	0·55	3·1
C_7	0·02	0·9

The tars produced during refining are of two types, acid tars and soda tars. The free acid, amounting to approximately 55%, is extracted from the former tar by repeated digestion with hot water and utilized in the manufacture of ammonium sulphate. This washed acid tar mixed with the soda tar is used as fuel. To burn this fuel efficiently requires special burners, and the tar lines must be heated or insulated. In a full refining scheme these tars, in conjunction with the dry gas, provide sufficient fuel to effect the various distillations involved.

Manufacture of Ammonium Sulphate

Essentially this process consists in liberating the ammonia from the ammonia liquor produced in retorting, combining it with sulphuric acid, collecting the ammonium sulphate so formed, and finally washing and drying this product. The ammonia liquor, which contains ammonia equivalent to 0·4 lb. of ammonium sulphate per gallon, is fed into the top of an 'ammonia still' which is simply a tower fitted with trays and bubble caps. As the liquor flows down the still, steam passes up removing the 'free' ammonia; the fixed ammonia, that is, the ammonia present as such salts as chloride and sulphate, is liberated by injecting milk of lime half-way up the tower. The steam and ammonia from the still pass into lead-lined vats containing sulphuric acid, recovered from the acid tar as indicated above, augmented by fresh acid. When the acid is neutralized the ammonium sulphate solution is settled, filtered, and transferred to a vacuum evaporator and concentrated. The crystals of ammonium sulphate which separate out are continuously removed, washed by a very weak ammonia solution, and dried first by centrifuging and finally by hot air. The finished product contains 99·8% $(NH_4)_2SO_4$ and must be free from acid and dry, otherwise difficulty in handling, storage, and transport is experienced through the crystals binding together in hard lumps.

REFERENCES

1. Abraham, H. *Asphalts and Allied Substances*, 2nd ed., 158 (1920).
2. Allan, D. *J.I.P.T.* **19**, 113 (1933).
3. Bailey, E. M. The Oil Shales of the Lothians. *Mem. of the Geol. Survey of Scotland*, 3rd ed., 173 (1927).
4. —— The Oil Shales of the Lothians. *Mem. of the Geol. Survey of Scotland* (1927).
5. —— The Oil Shales of the Lothians. *Mem. of the Geol. Survey of Scotland*, 190 (1927).
6. Beilby, G. *J.S.C.I.* **10**, 120 (1891).
7. Blackburn, C. O. *Quart. Colorado School of Mines*, **19**, no. 2, 12 (1924).
8. Bleloch, W. *J.I.P.T.* **17**, 521 (1931).
9. Botkin, C. W. *Quart. Colorado School of Mines*, **16**, no. 2, 22 (1921).
10. Challenger, F. *J.I.P.T.* **12**, 106 (1926).
11. Egloff, G. *Trans. Fuel Conference, World Power Conference*, **1**, 790 (1928).
12. Egloff, G., and Nelson. *J.S.C.I.* **51**, 326T (1932).
13. Francis, F. *J.C.S.* **125**, 381 (1924).
14. Francis, F., Watkin, C. M., and Wallington, R. W. *J.C.S.* **121** and **122**, 496, 1529, and 2804 (1922).
15. Franks, A. J. *Quart. Colorado School of Mines*, **16**, no. 4, 30 (1921).
16. —— *Quart. Colorado School of Mines*, **16**, no. 4, 33 (1921).
17. Garner, F. H. *J.I.P.T.* **14**, no. 70, 710 (1928).
18. Garret, F. C., and Smythe, J. A. *J.C.S.* **81**, 449 (1902) and **83**, 763 (1903).
19. Gavin, M. J. *U.S. Bur. Mines Bull.* no. 210, 99 (1924).
20. —— *U.S. Bur. Mines Bull.* no. 210 (1924).
21. Gavin, M. J., and Adyelotte, J. T. *U.S. Bureau of Mines Report*, no. 2313, 3 (1922).
22. George, R. D. *Colorado Geol. Survey, Bull.* no. 25 (1921).
23. Gray, T. *J.S.C.I.* **21**, 845 (1902).
24. Hellsing, G. *Arkiv. Kemi Mineral Geol. Stockholm*, **7**, no. 29, 23 (1921).
25. Henderson, N. M. B.P. 11,799 (1891).
26. Hentze, E. *Z. angew Chem.* **35**, 330 (1922).
27. Higgs, P. G. *J.I.P.T.* **21**, 135 (1935).
28. Holmberg, B. *Trans. Fuel Conference, World Power Conference, London*, **1**, 680 (1928).
29. Japanese National Committee. *Trans. Second World Power Conference*, **8**, 91 (1930).
30. McKee, R. H., and Goodwin, R. T. *Quart. Colorado School of Mines*, **18**, no. 1, 20 (1923).
31. McKinney, J. W. *J.A.C.S.* **46**, 968 (1924).
32. *Report of Newnes Investigation Committee.* Government Printer, Sydney (1934).
33. Robinson, G. C. *Trans. Roy. Soc. Edin.* **28**, 561 (1879).
34. Robinson, G. C., and Goodwin, W. L. *Trans. Roy. Soc. Edin.* **29**, 265 (1880).
35. Steuart, B. *J.S.C.I.* **19**, 986 (1900).
36. Steuart, D. R. Oil Shale of the Lothians. *Mem. of the Geol. Survey of Scotland*, 136–94 (1912).

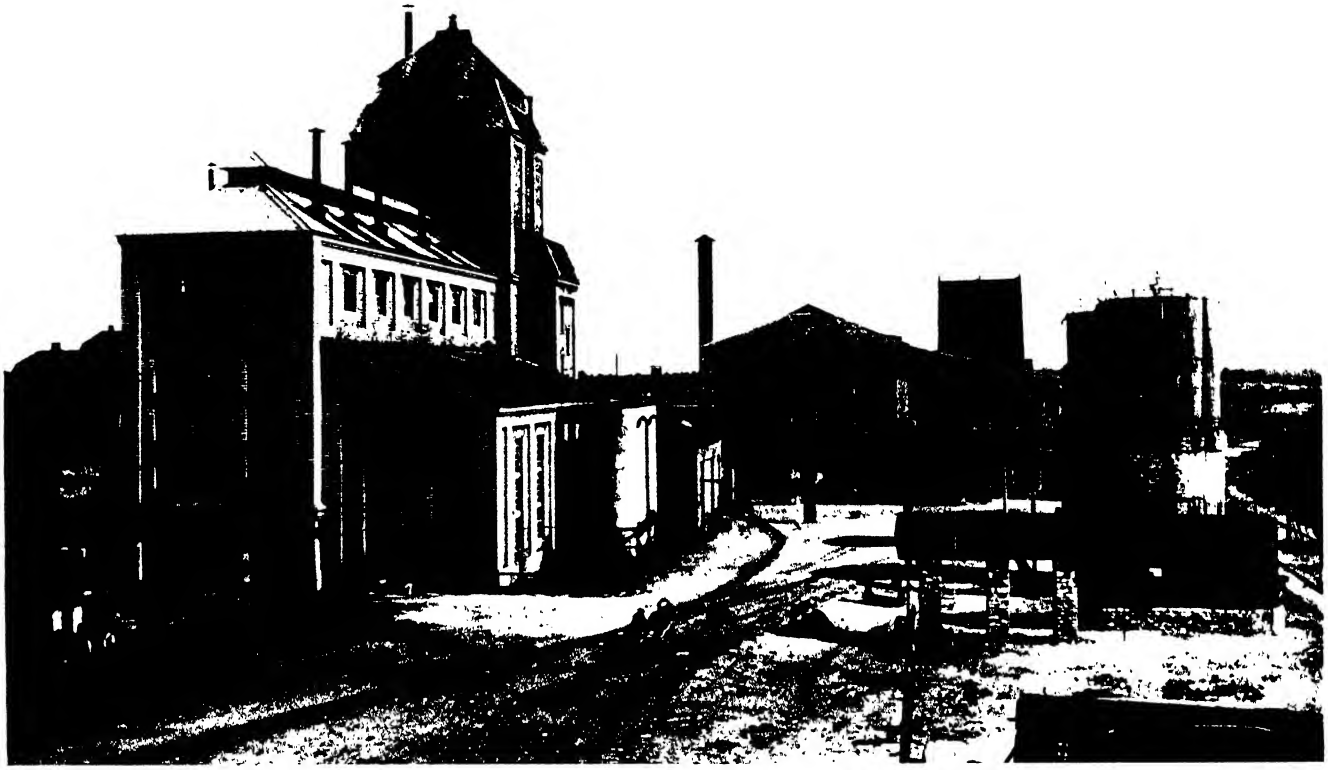


FIG. 2. Photograph of State Plant at Kohtla Järve

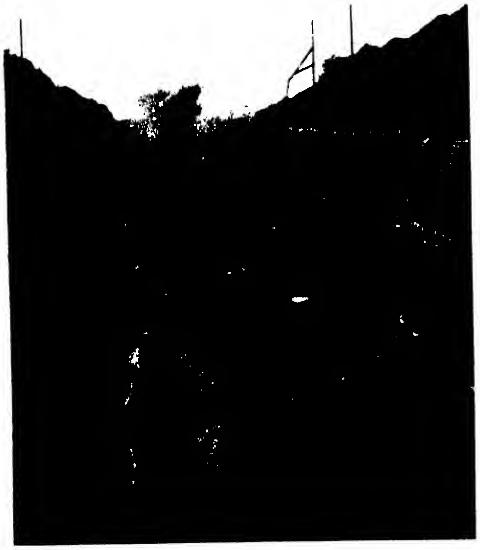


FIG. 1. Quarrying the oil shales

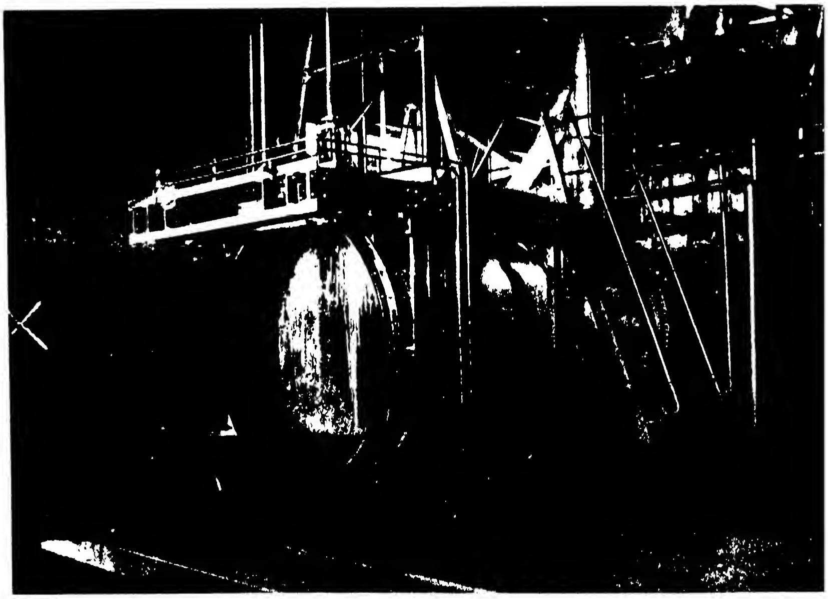


FIG. 3. Discharge end of the tunnel-oven at 'Kiviôli'

ESTONIAN SHALE OILS

By PROFESSOR PAUL N. KOGERMAN, D.Sc. Techn., D.I.C., M.Inst.P.T.

Rector of the Tallinn Institute of Technology, Estonia

The Oil Shales

In north Estonia two kinds of oil shales occur, i.e. in the north-west hard, black Dictyonema shale, in the north-east softer yellowish-brown, so-called 'kukersite'. The Dictyonema shale belongs to the Lower Ordovician (Tremadocian) strata; its seams are about 5 metres in thickness in the west, but they thin out towards the east (at Narva). The average percentage composition of the Dictyonema shale is as follows: SiO_2, 54·32%; Al_2O_3, 12·91%; Fe_2O_3, 0·22%; FeO, 1·61%; FeS_2, 4·49%; CaO, 0·61%; MgO, 1·08%; K_2O, 7·66%; P_2O_5, 0·14%; SO_3, 0·15%; S in org. compounds, 0·34%; H_2O of constitution, 1·36%; C, 9·41%; H, 1·10%; N, 0·65%; O, 3·82%. The yield of oil in the Fischer Apparatus (up to 575° C.) is 7·74% (including 56·2% of H_2O in the distillate) [17, 1928].

The shale has not been used so far for commercial production of oil.

TABLE I

Production of Oil Shale and Shale Oil (in metric tons)

	1925	*1926*	*1927*	*1928*	*1929*	*1930*	*1931*	*1932*	*1933*	*1934*
1. Total production of oil shale	288,104	413,719	397,609	446,118	517,642	497,955	499,494	501,805	499,969	588,958
2. Used for retorting	22,743	39,601	32,175	69,951	61,896	54,781	93,880	198,205	202,099	243,464
3. Crude oil obtained	3,118	5,784	4,291	11,866	11,286	10,006	17,052	36,595	37,617	46,877

For retorting and production of oil the rich oil shale 'kukersite' is used. The kukersite deposits occur in the Middle Ordovician strata, the whole formation attaining a total average thickness of 2·2 metres (excluding limestone) over an area of about 2,500 sq. km. Where the oil shale is typically developed, it consists of seven beds or seams, which are interstratified with limestone beds. Some of the oil-shale beds are highly fossiliferous. The colour of kukersite varies from greenish-yellow to reddish-brown. In thin section under a microscope the kerogen has an amber-yellow colour. The density of the mineral varies from 1·30 to 1·80. The average proximate composition of kukersite of first quality is as follows: moisture, 11·8; CO_2, 10·7; mineral ash, 35·6; total ash, 46·3, and organic matter about 42%. The calorific value of pure kerogen is about 8,900 cal./g., and the calorific value of the raw shale is about 3,500 cal./g.

The ultimate percentage composition of the organic matter varies within the following limits: C, 76·5–76·7; H, 9·1–9·2; N, 0·2–0·4; S, 1·6–2·2; Cl, 0·5–0·7; and oxygen (by difference), 11·1–12·2%; C/H ratio = 8·4. The solubility of the shale in ordinary solvents is very low and does not exceed 1·0% [5, 1922; 9, 1931].

In the early period of the shale-oil industry the shale was mined by open-cut or quarried; at present the greater portion of the shale is obtained from underground mines.

The production of oil shale and shale oil in Estonia for the last 10 years is given in Table I.

The data in Table I show the progress of shale-oil production in the last 10 years: in 1925 only 7·9% of the shale mined was used for production of oil; in 1934, in spite of the increase of raw-shale production, 41·3% of the shale was retorted in order to produce shale oil. An increase in the yield of crude oil from raw shale is noticeable as well.

The greater portion of the shale produced (about 300,000 tons) is still used as under-boiler fuel. Special types of grates have been developed for burning of the raw shale [11, 1935].

The first attempts to distil the shale on a semi-large scale were made during the World War. Many different types of retorts have been used for retorting of this shale, but only a few have been found suitable for commercial production of oil.

Retorting of the Shale

There are four distillation plants working at present. The oldest shale distillation plant in operation is that of the State Works at Kohtla. The plant consists of 6 retorts of the producer-type, designed by J. Pintsch & Co. (Berlin). The throughput of a single retort is about 33 to 35 tons per 24 hours, the temperature of retorting about 500 to 550° C.

(1) **The Pintsch Retort** consists of a vertical cast-iron shaft lined with firebrick. Its external diameter is 2 metres, and its height 5 metres. The shale is charged through a bell hopper in the usual manner, and then descends by gravity through the producer. The gases generated in the combustion chamber at the base of the producer in the lower part of the retort enter the annular flues at the top of the combustion zone and pass into the charge undergoing distillation. These gases, supplemented by cold permanent gas returned from the recovery plant, effect the distillation of the shale. The condensable volatile products leave at the top of the retorts, and pass successively through the cooler, exhauster, tar extractor, and condensers to the separating tanks.

(2) At the '**Eesti Kiviõli**' (Estonian Shale Oil) Company plant two retorts of the tunnel-kiln type are in operation. Each tunnel, circular in section, is about 45 metres long and about 2 metres in diameter. The tunnel is divided by sliding shutters into three sections: drying, carbonizing, and cooling. The shale is charged into steel tubs or wagonettes of rectangular form (2 × 1·2 × 1·2 metres). The tubs run on rails and are pulled mechanically through the tunnel. The tub is provided with a short flange pipe at the bottom. The shale rests on a false bottom or grid which allows the passage of volatile matter. In the main heating

flue running alongside the retort are placed vertical reheater tubes. The shale is heated by the volatile products of distillation. For this purpose there are provided at regular intervals along the tunnel flanged pipes of the same dimensions as those on the tubs. At each position in the tunnel the tub rests immediately above the circulation pipe. The volatiles are forced by means of an electrically driven fan through the charge, then through a duct at the top of the tunnel to a distribution channel above vertical reheater tubes. From the reheater tubes the gases pass via the circulating fan and a short duct at the bottom of the flanged pipes into the tub. The surplus gas escapes by the main gas-pipe to the condensing plant. The shale remains in the retort for about 2 hours. The throughput of a single retort is about 240 tons a day.

From the retort the oil vapours and permanent gases pass into the gas main, which conducts the volatile distillation products to air-cooled vertical condensers. In these condensers the heavy and medium oil separate from the lighter vapours and gases. The rest of the volatiles passes farther to the water-cooled condensers, and finally to the washers. The wash oil is cooled in a refrigerator to about −10° C. By this fractionating condensation three fractions are obtained: (i) mixture of heavy and medium oils, (ii) light oil, and (iii) crude benzine or motor spirit.

(3) In addition to these two systems of internally heated retorts an improved type of externally heated rotary retort is operated by the **New Consolidated Gold Fields Ltd.** The retort, designed by T. M. Davidson, of Patent Retorts Ltd. (London), consists of a steel shell, 75 ft. long and 4 ft. in diameter, supported on rollers, and having a slight inclination from the feed to the discharged end. The retort is rotated at a speed of 1 revolution in 1½ min. The interior of the retort is provided with scrapers which move to and fro longitudinally and prevent the accumulation of scale on the inner side of the shell. The feed of shale is continuous and automatic. In the passage through the retort the shale turns over many times, and the temperature of the charge is progressively raised until a final temperature of about 485° is reached. The volatile products are withdrawn through an offtake tube and pass into a dust-catcher situated near the discharge end of the retort. The hot residue is charged into a duct in which are fitted two valves (operated by compressed air) to regulate the feed into the heating furnace, on a special grate of which the residue is burnt. Operating in this way, the sensible heat of the residue is utilized in addition to its calorific power. To supplement the heat obtained from the residue, stripped gas is introduced at the back of the furnace. No external fuel is required to keep the distillation process going. A continuous run of a single unit for about 100 days is not uncommon. Two batteries of four Davidson retorts are now in operation. The daily throughput of a single retort is about 20 tons of shale [6, 1927; 14, 1930; 16, 1934; 23, 1933].

The Yield of Oil

As a criterion of efficiency of operation of a retort the factor of conversion of organic matter into crude oil is regarded by the author as the most reliable guide. On distillation in the 'Fischer aluminium apparatus' in the laboratory, from 65 to 70% of kerogen of a freshly mined unweathered shale is converted into oil. In the tunnel type of retorts and in the Davidson rotary retort the recovery of oil is about 88–92% of the 'Fischer yield'; in the case of Pintsch retorts the yield of oil is somewhat lower, i.e. about 78% of the Fischer yield; so, in the first case, about 47 gal. of oil is obtained per ton of run-of-mine shale or about 53 gal. per ton of dry shale of the average composition [10, 1934].

Properties of Crude Oils

At the 'Eesti Kiviõli' works and at the 'Estländska Oljeskifferkonsortiet' Ltd. plant, both of which have tunnel ovens (the latter plant has been redesigned recently), the system of fractional condensation is applied to remove the oil vapours from the permanent gases, and therefore no crude oil as such is obtained. In Tables II and III comparative data are given for some of the crude oils obtained on commercial retorting of the shale.

Table II

Properties of some Crude Oils obtained from Kukersite by Different Methods of Retorting

Oils	*A*	*B*	*C*	*D*	*Remarks*
Sp. gr. at 15° C.	0·946	0·950	1·002	0·939	..
Viscosity at 50° (Engler)	1·6	1·6	4·7	..	..
Flash-point (Pensky-Martens)	30°	21°	92°	14°	..
Unsaturation (1 vol. oil + 1 vol. benzine + 4 vols. of 80% H_2SO_4)	41	27	45	..	Vol. percentage given; average of two determinations
Alkali-soluble, vol. %	36	34	39	30·6	1 vol. of oil + 1 vol. of benzine + 2 vols. 10% NaOH
Moisture .	0·9	1·1	0·5	0·8	Water contents given in c.c. per 100 g. of oil.
Dust or free carbon, % by wt.	0·02	0·54	0·05	0·18	..
Yield of oil, % (approximate figures)	15	18–20	17–18	20–1	..

Description of Retorts

(*A*) Vertical modified Scottish retort, externally heated, superheated steam used also, internal temperature about 450° C.; (*B*) 'Fusion' retort; (*C*) J. Pintsch's producers; (*D*) Davidson rotary retort.

Table III

Engler Distillation of the Shale Oils

(*Amount of oil given in c.c.*)

Temp. °C.	*A*	*B*	*C*	*D*	
I.B.P.	*83°*	*80°*	*98°*	*85°*	*Remarks*
Up to 150	11·9	7·7	0·3	10·7	..
150–175 .	6·3	5·9	0·1	6·2	..
175–200 .	9·8	4·6	0·7	4·5	..
200–225 .	8·1	6·0	3·8	4·5	..
225–250 .	8·1	5·9	6·1	5·8	..
250–275 .	7·0	6·9	5·2	6·8	..
275–300 .	7·9	6·4	8·6	8·0	..
Over 300 .	43·3	58·6	75·5	58·7	Amount of residue left (b.p. over 300°) is given in per cent. by wt.
Amount of oil taken in grams	94·4	92·2	96·4	94·0	..

After the installation of benzine washers in 1932 the specific gravity of the Kohtla (State mine) crude oil decreased to 0·97–0·98 at 20° C.

Properties of unrefined oils from the tunnel retort are as follows:

1. *Mixture of Heavy and Medium Oils.*

Specific gravity at 15°	1·01
Viscosity at 50°	7·0–7·8° E.
Insoluble in normal benzine	about 10%
Mineral substances	0·01–0·02%
Moisture	6·4%

Engler distillation:

Up to 200°	1·0–2·0%
200–300°	16–17%
300–360°	44–52%

2. *Light Oil.*

Specific gravity at 15° C.	0·830
Sulphur	0·90%
Phenols	about 6·5%
Unsaturated compounds	about 30%

Engler distillation:

I.B.P.	64° C.
Up to 100°	2·0–3·0%
100–125°	8·0–10·0%
125–150°	13·0–15·0%
150–185°	17·0–23·0%
185–200°	7·6–8·8%
200–220°	10·4–12·0%
Residue (above 220°)	about 33%

3. *Crude Benzine (Gasoline); gas benzine not included.*

Specific gravity at 15° C.	0·767–0·770
Sulphur	0·72–0·74%
Unsaturated compounds	about 28%

Engler distillation:

I.B.P.	48° C.
Up to 100°	21·5–25·3%
100–125°	21·7–23·8%
125–150°	18·8–19·4%
150–185°	15·0–16·0%
185–200°	4·3–4·6%
200–220°	5·4–5·6%

Marketable Products

At present the most valuable product of the crude shale oil is motor spirit or benzine (gasoline). The other products are: (i) impregnating oils, (ii) Diesel oil, (iii) fuel oils, (iv) shale asphalts or bitumens, and minor products of the industry, e.g. phenolates, insecticides, &c. The main products of the State oil-shale industry prior to the installation of the cracking plant have been as follows:

1. 'Motornaphta', or Diesel oil, which is obtained from the crude oil by distillation. The distillate is neutralized and the lower boiling constituents removed by steam. The properties of this product are:

Flash-point (Pensky-Martens)	over 60° C.
Viscosity at 50° C.	1·0–1·3° E.
Specific gravity at 15°	0·93–0·95
Sulphur	about 0·9%
Coke (crucible-test)	3–4%
Calorific value	9,700–10,000 cal. per. g.

Distillation Test:

Up to 200° C.	5–8%
200–250° C.	15–20%
250–300° C.	20–30%
300–360° C.	30–40%

2. Pitch is the distillation residue of the crude oil and has a melting-point of 70 to 90° C. The properties of this product are dependent on the method of distillation.

A part of the crude oil is subjected at present to 'air blowing' to produce three grades of heavy oils and five grades of bitumen or blown asphalts.

3. Estobitumens A, B, C, D, and E. The blowing of the oil is carried out in stills of 8 to 10 tons capacity. The hot bitumen is passed into special tanks from which it is poured into barrels.

On blowing, about 10% of the crude oil is obtained as distillate and about 80% forms bitumen.

Properties of Estobitumens A, B, C, D, and E

Melting-points (Kraemer-Sarnow)	18–65° C.
Specific gravities	1·07–1·09
Solubility in CS_2	98·5–99·5%
Solubility in CCl_4	98–9%
Sulphur	0·9%
Mineral ash	0·3–0·5%
Flash-points	180°–220° C.
Coke	25–35%

The Estobitumens A, B, C are used in road-making as surfacing tars and asphalt mastic. The products which have higher melting-points are used in the manufacture of roofing paper. Some other products are also manufactured from bitumen.

4. Phenolate is obtained from crude oil by treating the oil with 5 to 10% caustic soda solution. The phenolate is used as disinfectant and for the preservation of timber and railway sleepers.

A certain amount of the crude oil is still treated on the same lines. Since 1930 a small cracking unit has been working in connexion with the Pintsch retorting plant. The oil is cracked in liquid phase under a pressure of about 40 atm. (585 lb.) at about 410° C. The yield of cracked benzine is about 13%. The asphalt-like residue is somewhat similar to the softer grades of blown bitumens.

The refining of light distillates consists of treatment with sulphuric acid and alkali-plumbite solution (at State works and 'Kiviõli'), and of treatment with sulphuric acid and caustic soda and nitrate solution (at the refinery of N.C.G.F. Ltd.). Three grades of benzine are produced: (i) light or avio-benzine (Estoline ABA), sp. gr. 0·735 at 15°/15°, F.B.P. 190°, boiling below 100°, 40%; (ii) ordinary motor spirit: the product of N.C.G.F. Ltd. is called 'Consoline', sp. gr. 0·747 at 15°/15°, 28% boiling up to 100°, and that of 'Kiviõli' 'Estoline ABI', sp. gr. 0·740–0·750, F.B.P. 200°; and (iii) heavy benzine, sp. gr. 0·789, for blending and as tractor fuel.

The octane number of avio-benzine is 75–7, and that of the ordinary grade about 70–4.

Cracking and Hydrogenation

The crude shale oil has been cracked by various systems of cracking. The Dubbs process yielded 42·7% of benzine, 200° end-point, of 73 octane number, on cracking of N.C.G.F. Ltd.'s crude [2, 1933]. Somewhat higher yields of benzine were obtained from the same crude by the Carburol process.

The hydrogenation of kukersite oils on a laboratory scale has been studied both in Estonia and in the U.S.S.R. Up to 70% of gasoline has been obtained from the crude oil by repeated hydrogenation [12, 1932; 15, 1927; 18, 1932].

Chemical Composition of Crude Shale Oil and its Products

The elementary composition and calorific value of crude oils are given in Table IV below:

TABLE IV

Elementary Composition of Crude Oils

Company	*Sp. gr. 20°/15°*	*Composition %*				*Calorific value cal. per g.*
		C	H	O+N	S	
N.C. Gold Fields Ltd.	0·940	82·9	10·6	5·8	0·7	9,750
'Kiviõli' A.-Ü. .	0·945	83·6	10·6	5·2	0·6	9,830
State Works .	0·998	83·0	9·7	6·4	0·9	9,455

The mean molecular weight of the crude oil in benzene is about 270.

The 'synthetic crude' of Kiviõli was obtained on mixing the fractions in proportion corresponding to the actual yield of cuts on fractional condensation. The gas benzine is not included in the crude oil of 'Gold Fields'.

The nitrogen content of the State Works' crude oil is 0·25%, and of other elements, traces of chlorine (0·1%) have been found in the oil.

As an average a crude oil contains: neutral compounds 74·5%, phenols 22·5%, acids 2·8%, and bases 0·2%. Only traces of paraffin wax have been found in the crude oil, which is a typical asphalt-base oil.

The percentage distribution of phenols and acids in fractions of crude oil is given in Table V.

TABLE V

Distribution of Phenols and Acids in Shale Oil

Boiling range under 8 mm. Hg, °C	*Phenols, %*	*Acids, %*
150–175	19·4	2·1
175–200	26·5	5·2
200–225	31·9	1·7
225–250	35·2	1·5
250–275	22·7	1·4
275–300	18·9	1·4

The percentage of phenols seems to be highest in the fraction 350–375° (atm. pressure), amounting to about 10% of the crude [16, 1934].

The distribution of sulphur and bases in the fractions of crude oils is given in Table VI.

TABLE VI

Distribution of Sulphur and Bases in Crude Oils

Fractions, °C.	*Sp. gr.*	S, %	*Bases, %*
Up to 175	0·7557	1·26	0·18
175–200	0·8438	1·11	0·42
200–225	0·8808	1·08	0·48
225–250	0·9224	0·97	0·52
250–275	0·9509	0·80	0·59
275–300	0·9589	0·74	0·38
300–325	0·9589	0·78	0·16
325–350	0·9904	0·78	0·08

The percentage of sulphur is highest in the light fractions of all crude shale (kukersite) oils: the fraction of light oil b.p. 140–170° contains 1·5% of S. The bases have been determined in the fractions of the State Works' crude oil, whereas the sulphur was determined in fractions of a crude oil obtained on small-scale distillation, but this does not alter to any considerable extent the values in Table VI [22, 1925; 4, 1927].

Hydrocarbons

The chemical nature of lower boiling fractions only has been studied thoroughly; no individual compounds have been isolated from higher boiling fractions of shale oil. In the lower boiling fractions the unsaturation increases almost in parallel with the rise of boiling-point. In the case of an unrefined light oil from tunnel-retort the fraction boiling up to 70° contained: 25·4% of unsaturated and 12·7% of aromatic compounds, the fraction 100–105°, 29·2% of unsaturated and 15·3% of aromatic compounds, and the fraction 170–175°, 24·8% of unsaturated and 13·1% of aromatic compounds. Of saturated (normal) hydrocarbons the following have been isolated from the light shale oil: C_6H_{14}, C_7H_{16}, C_8H_{18}, C_9H_{20}, $C_{10}OH_{22}$. The presence of naphthenic hydrocarbons in the shale oil has been reported [1, 1932].

The elementary composition of a shale gasoline, sp. gr. 0·7129 at 20°/15°, has been found to be as follows: C, 85·3%, and H, 14·26%, which corresponds to a formula C_nH_{2n}.

Some data on the composition of higher fractions of the neutral oil (a crude oil from which the acids, phenols, and bases have been removed) are given in Table VII below.

As is evident from Table VII, the higher fractions of the shale oil contain some neutral oxygen compounds; qualitative reactions have proved the presence of ketones [3, 1930].

Phenols

Only traces of phenol, C_6H_5OH, have been found in the oil. From the fraction of the crude oil, b.p. 230–270°, *o*-,

TABLE VII

Composition of Higher Fractions of Neutral Oil

Fractions under 8 mm. Hg, °C.	*Sp. gr. at 15° C.*	*Solubility in H_2SO_4, vol. %*	*Solubility in dimethyl-sulphate, vol. %*	*Ultimate composition %*					*Mol. weight*	*Per cent. of asphaltic matter*	*Iodine value*	*Per cent. of coke*	*Viscosity at 50° C. (Engler)*
				C	H	S	Cl	O					
150–175	0·9082	45·9	29·3	85·35	11·51	1·03	0·15	1·96	197	..	114·2	0·22	1·80
175–200	0·9515	62·5	41·4	84·19	10·49	1·11	0·21	4·00	234	..	131·2	0·26	1·48
200–225	0·9854	69·2	40·5	84·03	9·92	1·09	0·26	4·70	271	0·03	98·7	0·44	3·23
225–250	1·0020	75·6	39·3	84·09	9·98	1·15	0·29	4·49	283	0·19	111·3	1·08	6·90
250–275	1·0126	89·2	26·7	84·36	9·87	0·97	0·21	4·59	330	0·15	128·2	1·82	23·5
275–300	1·0218	93·5	20·6	84·33	9·71	0·69	0·18	5·09	352	0·23	120·4	4·78	41·6

m-, and *p*-cresols, and 1 : 4 : 2-, 1 : 3 : 4-, and 1 : 2 : 4-xylenols have been isolated. Of cresols the *m*-isomer predominates [7, 1927; 19, 1924].

The presence of phenol ethers of guaiacol type in the oil has been proved.

The crude phenols and phenoxides possess a high disinfecting power, and have proved to be suitable for impregnating timber, &c. [20, 1929; 21, 1926].

Acids

The acid content of two fractions of shale oil has been investigated: (i) the fraction boiling up to 200°/90 mm. Hg with about 2% of acids, and (ii) the fraction b.p. 175–225°/40 mm. Hg which contains about 2·4% of acids.

The mixture of acids of the first fraction is an oily reddish-brown liquid having a smell of lower fatty acids. Its properties are as follows: sp. gr. 0·964; *n*, 1·4517; I.B.P. 173°; about 70% of acids distils below 250°. Of the mixture 87·8% is soluble in petroleum ether (A), of which 29·7% is volatile with steam (C), and 70·3% non-volatile (D). The fraction C contains 29·3% of water-soluble acids (H) and 70·7% of non-soluble acids (G). Of the portion insoluble in petroleum ether, 3% is volatile with steam (E), and 97% is non-volatile with steam (F).

The composition of these fractions is given in Table VIII.

TABLE VIII

Ultimate Composition of Acids

Fractions (see scheme above)	Average C %	Average H %	Iodine value	Mean mol. wt.
A	66·11	10·39	53·4	136·3
D	67·33	10·10	. .	145·2
E	. .	. .	170	} 84·0
F	. .	. .	64·5	
G	62·69	10·39	38·2	115·1
H	60·83	9·73	43·0	110·9
Mixture of acids	66·14	9·74	72·6	131·2

The acids of the second fraction, i.e. b.p. 175–225°/40 mm., form a dark reddish viscous liquid of sp. gr. 1·0374/20°, the iodine value of the acids was 85·3, and their composition was: C, 71·34%, H, 10·76%, O, 17·84%. About 45% of the acids is volatile in steam; the steam-distilled acids have a peculiar odour and yellow colour; they contain C, 68·42%, H, 10·76%, O (by diff.), 20·82%. The non-volatile acids are consequently richer in carbon. Properties of these acids are shown in Table IX below.

The acids of kukersite oil seem to be chiefly saturated and unsaturated aliphatic acids.

Bases

The pure bases separated from the shale oil form a reddish liquid, with a quinoline-like odour, sp. gr. 0·9731 at 15°, *n*, 1·539/19°. The mean ultimate composition of the bases was as follows: C, 81·54%, H, 9·59%, and N, 8·59%. The bases belong to the derivatives of pyridine and quinoline [8, 1930].

Gum Formation and its Prevention

Because of the unsaturated character of kukersite oils the problems of autoxidation and gum formation have been studied to some extent. It is worthy to mention that the formation of crystalline oxidation products in light oils along with the formation of liquid gum has been observed [8, 1930].

Many inhibitors have been applied with success for the stabilization of benzines.

Physical Properties of the Oils

The most important physical constants of crude shale oils and their fractions have been determined. Some of the values are given in Table X [13, 1930]:

TABLE X

Coefficients of Expansion, Specific Heats, Latent Heats of Vaporization, and Surface Tensions of Shale Oils

Fractions, °C.	Mean coeff. of expansion	Sp. heat 20° C.	Latent heat of vaporization, cals.	Surface tension σ_{20} mg./mm.
Up to 150 .	0·0009712	0·552	70·8	2·802
150–175 .	0·0009523	} 0·548	69·0	2·824
175–200 .	0·0009393		69·8	2·818
200–225 .	0·0009027	0·504	68·4	2·876
225–250 .	0·0008677	0·507	60·4	2·931
250–275 .	0·0008226	0·500	60·2	2·899
275–300 .	0·0007716	0·502	56·4	2·868
Kohtla crude oil	. .	0·504	. .	3·38
Davidson crude oil	. .	. .	. .	2·88

Summarizing the data obtained on chemical investigation of kukersite oils, one may come to the following conclusions: (i) the majority of compounds present in kukersite oil have been isolated also from normal crude petroleum. The neutral compounds of kukersite oil (chiefly hydrocarbons) correspond closely to the neutral constituents of petroleum, especially to those found in asphalt-base oils; (ii) on the other hand, the crude shale oil contains many constituents which are also found in low-temperature coal tars, viz. cresols, xylenols, unsaturated hydrocarbons, &c.; (iii) but in addition to this the shale oil contains many constituents which so far have not been found in low-temperature coal tars, viz. phenolic ethers, polyphenols, fatty acids, &c. The shale oil might be regarded as a source of raw materials for the chemical industry in the future.

TABLE IX

Properties of Acids of the Fraction 175–225°/40 mm.

Fractions, °C., 120 mm. Hg	Specific gravity at 17° C.	Refractive indices at 17° C.	Acid numbers	Iodine numbers	Average empirical formula	Basicity calc.	Per cent. of acids, Ag-salts soluble	Iodine numbers of acids in the previous column
200–210	0·9667	1·4637	352·9	59·2	$C_{8\cdot9}H_{17\cdot9}O_2$	1·02	16·8	67·3
210–220	0·9808	1·4749	333·0	65·5	$C_{9\cdot8}H_{18\cdot7}O_2$	1·01	15·8	85·6
220–230	1·0030	1·4886	304·5	68·4	$C_{10\cdot8}H_{20\cdot5}O_2$	. .	17·2	93·4
230–240	1·0193	1·5051	294·6	72·2	$C_{11\cdot3}H_{21\cdot3}O_2$	0·97	17·3	98·4
240–250	1·0304	1·5105	273·2	81·3	$C_{12\cdot5}H_{22\cdot5}O_2$	1·03	18·2	108·1
250–260	1·0446	1·5261	250·3	105·7	$C_{13\cdot7}H_{25\cdot5}O_2$	0·96	18·5	133·7

APPENDIX

During the years 1935–6 the shale oil industry has undergone a rapid expansion:

(i) Eight new retorts of simplified Pintsch-type have been erected at the State plant at Kohtla, giving an additional throughput of about 300 tons of shale per 24 hours.

(ii) Two more tunnel ovens have been added to the existing plant of 'Kiviõli', each capable of treating about 400 tons of shale a day.

(iii) The Swedish plant of the 'Estlänska Oljeskiffer-konsortiet' at Sillamägi, which had been standing idle for many years, was redesigned and reconstructed, and is now again in operation.

The production of oil shale in 1936 was 766,410 tons, and the production of shale oil 63,456 tons.

REFERENCES

1. Dubov, P. I., and Chelintzev, V. V. (Editors). *Treatise on Oil Shales and their Technical Utilization* (in Russian), p. 283 (1932).
2. Egloff, G., and Nelson, E. F. *Oil and Gas J.* **31** (34), 14 (1933).
3. Hüsse, J. *Sitzungsberichte d. Naturforscher-Gesellschaft zu Tartu*, **36**, 13 (1930).
4. Klever, H., and Mauch, K. *Über den estländischen Ölschiefer 'Kukkersit'*, Halle (1927).
5. Kogerman, P. N. *Acta et Comment. Univers. Tartuensis*, A. **3**, 6 (1922).
6. —— *The Oil-Shale Industry of Estonia*, Tartu (1927).
7. —— *J.S.C.I.* **46**, 14 (1927).
8. —— *Trans. 2nd World Power Conference*, **8**, 33–42 (1930).
9. —— *Archiv für die Naturkunde Estlands*, I S., X Bd., 2 Lief. (1931).
10. —— *L'Energia Termica*, no. 3 (1933) and no. 1 (1934).
11. —— *Die Naturwissenschaften*, **19**, 301–5 (1935).
12. Kogerman, P. N., and Kopwillem, J. *J.I.P.T.* **18**, 833–45 (1932).
13. Kogerman, P. N., and Kõll, A. *Sitzungsberichte d. Naturforscher-Gesellschaft zu Tartu*, **37**, 3/4 (1930).
14. Kogerman, P. N., and Roberts, J. *Trans. 2nd World Power Conference*, **8**, 110–26 (1930).
15. Kopwillem, J. *Beitrag zur Untersuchung d. estländischen Schieferöle.* Inaug. Dissert. Zürich (1927).
16. Luts, K. Der estländische Brennschiefer-Kukersit, seine Chemie. Technologie und Analyse, Tartu (1934).
17. Rägo, N. *Acta et Comment. Univers. Tartuensis*, A. **13** (1928).
18. Waterman, H. I., de Jong, S. C., and Tulleners, A. J. *J.I.P.T.* **18**, 183–6 (1932).
19. Weiderpass, N. *Pharmacia*, Suppl. 1/2 (1924).
20. —— *Sitzungsberichte d. Naturforscher-Gesellschaft zu Tartu*, **35** (1929).
21. Weiderpass, N., and Kogerman, P. N. Ibid. **33** (1926).
22. Wittlich, M. *Acta et Comment. Univers. Tartuensis*, A. **8**, 6 (1925).
23. Zeidler, R. *Neue Wege der Verwertung des Ölschiefers und seiner Umwandlung in Öle*, Tallinn (1933).

LOW-TEMPERATURE TAR OILS

By J. G. KING, Ph.D., A.R.T.C., F.I.C.
Chief Chemist, Fuel Research Station, Greenwich

THE yield, and to an extent the chemical nature, of low-temperature tar is affected by the type of carbonization process used. By low-temperature carbonization, however, is inferred a process in which the coal is not heated to a temperature greatly in excess of 600° C., so that the tars as a class differ markedly from those produced in the high-temperature carbonization processes of gas and coke manufacture. Low-temperature tars differ in properties according to the type of coal carbonized and the carbonization system used, but these differences are small in comparison with their divergence as a class from high-temperature tars. The greater proportion of low-temperature tar is made by one process only, but, owing to the attention which has been paid to experimental plants, a good deal of information is already available as to the properties of tars produced by a number of other processes.

Yield of Tar Oil from Coal

The yield of tar and therefore of tar oil is influenced by the temperature of carbonization, the nature of the coal, and the type of retorting system. The influence of temperature in one retorting system has been investigated at the Fuel Research Station [5, 1931] using three bituminous coals of widely different character. The yield of tar was found to reach an optimum at about 550° C. in each case. In order to illustrate this the results obtained with coal from the Barnsley seam [5, 1931] are given in Table I, calculated to yields per 100 parts of dry, ash-free coal. The yield of tar increases from 4·2% at 400° C. to 8·7% at 550° C., and then decreases to 8·2% at 600° C. The pitch content of the tars increases from 25·2 to 34·7 and 40·7%, so that the yield of tar oil shows the same definite optimum as the yield of tar.

TABLE I

Influence of Temperature of Carbonization on the Yield of Tar and Tar Oil

(per cent. by weight of ash-free dry coal. 'Dalton Main' Coal—Barnsley Seam)

Temperature, ° C.	*400*	*450*	*500*	*550*	*600*	*650*
Total tar	4·2	6·0	7·6	8·7	8·2	7·4
Sp. gr. at 15° C. . .	0·96	0·98	0·99	1·02	1·04	1·08
Oil to 170° C. . . .	0·45	0·60	0·68	0·52	0·52	0·62
Oil 170–360° C. . . .	2·83	3·57	4·82	5·29	4·72	3·76
Pitch and loss . . .	0·92	1·83	2·10	2·89	2·96	3·04

The other two coals behave similarly; in fact the yield curves of tar, tar oil, and tar acids have the same general shape for all three coals. The curves for the 'Dalton Main' coal only are shown in Fig. 1. The optimum points for tar, tar oil, and tar acids occur about the same temperature (550° C.). The yield of tar spirit decreases above 700° C. to a low figure. The pitch content of the tar increases steadily, but the amount produced shows a maximum between 600 and 700° C., owing to the decrease of tar yield above this temperature. In order to realize a high yield most systems of low-temperature carbonization operate at a temperature of 550–650° C. The yields of tar and tar oil at the optimum temperature from the three coals examined were as follows, per cent. of dry, ash-free coal.

Coal	*Parkgate*	*Barnsley*	*Warwick Slate*
Oxygen content, % . . .	5·2	6·8	12·8
Tar yield, %	9·0	8·7	10·1
Tar oil, %	6·5	5·8	7·6
Tar acids, %	1·66	1·71	3·01

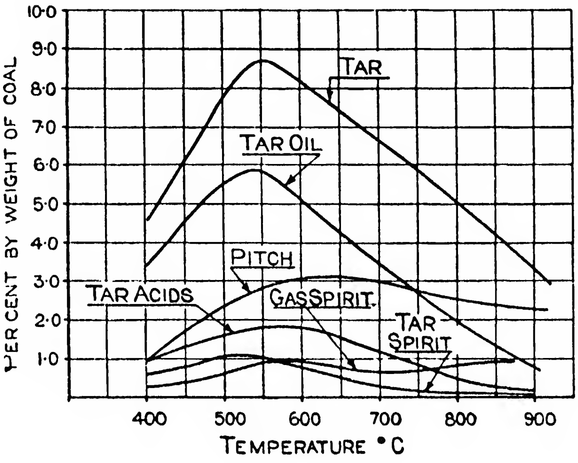


FIG. 1. YIELDS OF TAR PRODUCTS AT DIFFERENT TEMPERATURES OF CARBONISATION FROM DALTON MAIN COAL

Speaking generally, bituminous coals of higher oxygen content tend to give higher yields of tar oil owing to the greater amount of tar acids produced. If the comparison be widened to include other types of coal, a general conclusion is arrived at that the yield of tar increases with the percentage of volatile matter in the coal. Particularly high yields are obtainable from certain special types of coal such as cannel. The nature of the tar oil also varies with the type of coal; perhaps the most important variation is the increase in the proportion of tar acids with increasing oxygen content. The Warwick Slate coal, containing 12·8% of oxygen, yields 3·01% of tar acids, and the Parkgate coal (oxygen 5·2%) only 1·66%.

These differences, which can be attributed to the coal, tend to confuse any comparison which can be made of the effect of different retorting systems in that the data available refer in every case to a different coal. Low-temperature carbonization processes can, however, be classified into types, and an idea of the kind of tar to be expected from each type can be obtained from the results of tests by the Fuel Research Board, due allowance being made for simultaneous variation of the type of coal used. The data from five types of plant are given in Table II.

Taking all the above factors into consideration, it may

TABLE II

Effect of Carbonizing Plant on Tar Produced

Plant	*Parker*	*Fuel Research Station*	*Maclaurin*	*Turner*	*'L. & N.' British Coal Distillation Co. Ltd.*
Method of heating	External	External	Internal, using gas	Internal, using steam	Internal, using gas
Coal charge	Static	Continuous	Continuous	Continuous	Continuous
Approximate temperature of carbonization, ° C.	650	600–650	300 (top)–1,000 (btm.)	590	670
Coal used	'Dalton Main' (S. Yorkshire)	'Dalton Main (S. Yorkshire)	Virgin seam (Scotland)	Ell seam (Scotland)	Mixture of Nether Lount, Middle Lount, Upper Roaster, Lower Roaster seams (Leicestershire)
Oxygen content of coal, % of ash-free dry coal	6·8	6·8	10·3	11·1	12·6
Dry tar, % by wt. of a-f-d-coal	8·8	9·1	8·4	9·7	6·0
Gas spirit, ,, ,,	0·6	0·5	0·5	0·7	0·5
Tar oil, ,, ,,	4·5	5·3	5·4	6·2	2·5
Pitch, ,, ,,	4·3	3·8	3·0	3·5	3·5
Tar acids, ,, ,,	1·5	1·0	2·0	..	..

be deduced that, from the type of coal which will be most commonly used for low-temperature carbonization, a yield of tar of 18·5 gallons per ton of dry, ash-free coal may be expected. In addition, about 2·0 gallons of spirit will be recoverable from the gas by washing. This total yield of 20·5 gallons is divisible into

	Gal.
Gas spirit	2·0
Tar spirit to 170° C.	1·5
Tar oil 170–360° C.	10·5
Pitch	80·0 lb.

Special outlets for tar products have been suggested by the researches of G. T. Morgan [9, 1932] who has shown (1) that satisfactory synthetic resins can be made from low-temperature tar phenols, (ii) that the phenolic fraction of high boiling-point is a good wetting agent for such purposes as the mercerization of cotton, and (iii) that the 'resinoids', which amount to about 7% of the tar, form a suitable base for paints, stains, and lacquers.

Motor Spirits

As shown above, low-temperature carbonization processes make available up to 3·5 gallons of crude spirit. This spirit corresponds to the crude benzole produced by high-temperature carbonization processes, but differs from it markedly in composition. The Fuel Research experiments [5, 1931] have shown that the gas spirit is greatly altered by the temperature of carbonization.

Percentages by weight

Carbonizing temperature, ° C.	*500*	*550*	*600*	*650*
Unsaturated hydrocarbons	28	31	20	22
Aromatic ,,	14	19	37	42
Saturated ,,	58	50	43	36

Between 550 and 600° C. the proportion of aromatic hydrocarbons begins to increase rapidly. The proportions of benzene and toluene at 500° C. are 7·1 and 4·4 respectively, while at 650° they are 24·3 and 14·0. Since this is the normal temperature used in low-temperature carbonization processes it will be realized that the composition of low-temperature spirits may vary widely. The proportion of unsaturated hydrocarbons decreases as the temperature rises.

Variations of composition are also caused by the type of coal used, but these are less marked. The range in six coals examined in Fuel Research experiments is

	L.-T. gas spirit	*L.-T. tar spirit*	*Blend*	*Petroleum spirit*
Aromatic hydrocarbons	16–30	33–52	24–40	22
Unsaturated ,,	20–42	16–38	18–40	3
Saturated hydrocarbons	38–51	24–31	34–43	75

The high percentage of unsaturated hydrocarbons makes the crude spirits unstable even in the dark, the freshly distilled spirit rapidly assuming a dark-brown colour and depositing a brown gum. The spirits are, however, amenable to refining by the ordinary process of washing with sulphuric acid and water. D. Hicks and J. G. King [6, 1931] have examined the spirits produced by the Fuel Research process of continuous carbonization in a vertical retort. The maximum temperature of carbonization was 625° C.

Although the spirits recovered from the gas and from the tar by distillation might be marketed as a blend, they were examined separately in this research. Satisfactory spirits were produced by washing with caustic soda to remove dissolved hydrogen sulphide and small amounts of phenols, with sulphuric acid of 80% strength, water, caustic soda again, and finally with water. In the case of gas spirit it was usually necessary to use acid in two stages, the first stage sometimes being of 60 to 70% strength, in order to avoid overheating. During the final distillation of the refined spirits some were found to colour if heated above 130° C., while steam distillation at 100° C. gave a water-clear spirit.

Despite the high proportion of unsaturated hydrocarbons in the spirits the loss on refining is not excessive, since only a small proportion of these, probably the diolefines, must be removed. The losses, 16% for gas spirit and 13·5% for tar spirit, are, however, high in comparison with those for petroleum spirit. The constituents, other than the phenols, which are removed are shown by the following analyses to be mainly unsaturated hydrocarbons with less than 2 % aromatic hydrocarbons.

Effect of Refining on Crude Low-temperature Spirit

(per cent. by weight of *crude* spirit)

	Unsaturated hydrocarbons	*Aromatic hydrocarbons*	*Saturated hydrocarbons and naphthenes*
Crude gas spirit .	46·0	16·4	37·6
Refined gas spirit	37·6	14·6	37·6
Crude tar spirit .	41·8	36·5	21·7
Refined tar spirit	29·2	37·6	21·7

The refined spirits form a blend which is a satisfactory fuel for the internal combustion engine. The more volatile spirit has been shown to be suitable for aviation purposes. The freshly refined spirits contain no dissolved gum, but during storage gum forms steadily, reaching about 30 mg. per 100 ml. after about 200 days, but without change of colour. Peroxide formation also takes place on storage to the extent of about 0·006 g. of oxygen per 100 ml. spirit in 200 days. The peroxide formation takes place in the gas spirit only.

In the Fuel Research experiments the H.U.C.R. of certain spirits was examined during storage in glass. The ratio decreased from an average of 7·3 (octane number $>$ 90) by about 0·4; in the same period petroleum spirit would show a negligible decrease.

The properties of typical spirits in comparison with a petroleum spirit are given in Table III.

TABLE III

Properties of Low-temperature Carbonization Spirits

	B.P. No. 1 petrol	*L.T. tar spirit*	*L.T. gas spirit*
Ultimate analysis:			
Carbon	86·06	88·55	87·26
Hydrogen . . .	13·78	11·41	12·74
Specific gravity:			
0° C.	0·753	0·840	0·776
15° C.	0·739	0·825	0·763
30° C.	0·729	0·809	0·751
Engler distillation (I.P.T.). Distillate up to—			
75° C.	13·5 ml.	..	10 ml.
85° C.	..	..	28 ml.
95° C.	..	..	45 ml.
100° C.	44·5 ml.	..	55 ml.
110° C.	..	..	70 ml.
120° C.	63 ml.	7 ml.	83 ml.
130° C.	..	29·5 ml.	..
140° C.	..	60·0 ml.	96 ml.
150° C.	86·7 ml.	82·0 ml.	..
160° C.	..	93·0 ml.	..
170° C.	..	98·7 ml.	..
175° C.	95·5 ml.	..	..
F.B.P.	183·5° C.	172° C.	158° C.
Residue	1·5 ml.	..	..
Calorific value (constant volume) (cal. per g.) . .	11,244	10,717	10,928
Total heat from 15° C. (cal. per g.)	127	122	106
Mean specific heat (15° C. to 25° C.)	0·486	0·360	0·445

The greater volatility of the gas spirit is evident; it has a lower specific gravity and carbon content, and a distinctly lower total heat per gram. In a normal blend it may be taken that the proportions would be 3 : 2 by volume, the gas spirit being the greater.

Tar Oils Boiling above 170° C.

Unlike the high-temperature tar product of the same boiling range, low-temperature tar oil (b.p. 170–360°) is fluid at atmospheric temperature and contains only a very small amount of crystallizable solids such as naphthalene. It may, however, contain quite a large proportion of solid paraffins, from 3 to 6 %, which crystallize when the oil is cooled to 0° C.

There are three ways in which the entire fraction can be utilized, (*a*) as a boiler fuel direct, (*b*) as a Diesel engine fuel direct, and (*c*) as a neutral oil for Diesel engines, after removal of the tar acids.

In order to prepare a boiler fuel from low-temperature tar it is necessary only to remove the spirit fraction to 170° C. and aerate the residue during cooling to remove traces of cracked products. The flash-point is thereby easily raised above 175° F. The heavy residue is a satisfactory boiler fuel, although owing to its tar-acid content its calorific value is only 17,000 B.Th.U. per lb. in comparison with 19,000 for petroleum fuel oil. Its high specific gravity, however (1·06), gives it a higher value on a volume basis. Under conditions, as in shipping, where the same fuel tanks would have to be used for both petroleum oil and tar its use would be prohibited, since petroleum oils, when mixed with tar, precipitate from it asphaltic or pitchy material as a heavy gummy residue. Under these conditions only tar distillates completely miscible with petroleum are admissible. The properties of typical oils from four processes are shown in Table IV in comparison with a good petroleum oil.

TABLE IV

Low-temperature Carbonization Fuel Oils

	A	*B*	*C*	*D*	*Petroleum oil*
Specific gravity at 15° C. . .	1·011	0·955	1·015	0·988	0·87
Flash-point, ° F. .	188	202	198	190	168
Viscosity at 60° F. . Redwood No. 1. sec. . .	85	26	175	119	30
Gross calorific value, B.Th.U. per lb. .	16,930	..	16,800	16,780	19,750
Gross calorific value, therms per gal. .	1·710	..	1·705	1·660	1·717
Water, % . .	1·12	0·45	0·95	1·17	0·0
Ultimate analysis:					
Ash . . .	0·03	0·03	0·02	0·03	0·0
Carbon . .	82·18	..	81·35	79·10	86·3
Hydrogen . .	8·89	..	9·17	9·86	12·8
Sulphur . .	0·74	..	0·70	0·94	0·9
Nitrogen . .	0·84	..	0·86	0·73	0·0
Difference (O_2 and errors) . .	7·32	..	7·90	9·34	0·0
Tar acids, % .	37·2	44·0	..	..	0·0

From 1927 to 1932 the British Admiralty has experimented with oils of this type [3, 1933].

It was found that a Fuel Research oil could be burned satisfactorily by a 900 lb. per hour sprayer, but only after reducing its water content by separation to 0·7%. An oil containing 2% of water gave trouble with pulsations. The boiler efficiency was as high as with Texas oil and the oil was miscible with petroleum oils. Following this success a specification was drawn up and oils from a number of processes were examined. Where the oil conformed to the specification it was found to be satisfactory. The provisional specification and the results of examination of a typical oil are given in Table V.

The pitch content quoted is the residue on distillation so that the true pitch content is appreciably less. Mixtures of the oil with petroleum oil in the ratio of 2: 1, 1: 1, 1: 2

TABLE V

Admiralty Specification for Low-temperature Tar Oil

	Specification	*Typical tar oil*	*Neutral tar oil*
Flash-point °F., Pensky-Marten	not < 175	186	178
Sulphur, %	not > 1·0	0·73	0·85
Inorganic acidity	free	nil	nil
Anthracene and sediment	sensibly free	trace	trace
Tar acids, %	not > 35	27	2·0
Water, %	not > 0·5	1·12	0·1
Viscosity (Redwood II at 32° F.), sec.	not > 1,000	25	130
Pitch, %	not > 2	2·2	2·1
Solids separating at 32° F. in 7 days, %	not > 0·1	..	0·01
Materials likely to choke burners	free	..	..
Calorific value, B.Th.U. per lb.	..	16,930	17,800

were stable on storage. Certain tar oils tend to form a waxy scum on storage; this is prevented by the addition of 3–10% of fuel oil in which the scum dissolves.

An oil of this type behaved satisfactorily under a boiler, giving an efficiency of 74·8% in comparison with Texas oil 74·2%.

Later a batch of tar oil was examined from which the tar acids had been removed, i.e. a neutral oil. The removal of the tar acids effected an appreciable increase of calorific value (1% acids = 35 B.Th.U.). This oil was also burned under a boiler with complete satisfaction, so much so that the Admiralty burned as much as 3,000 tons during 1933. The composition of an oil of this type is also shown in Table V.

These results show that low-temperature carbonization oils form suitable fuels for boiler purposes, but for general use they should be distillates since the presence of pitch limits their use. The tar acids need not be removed. A comparison of storage capacity in terms of heat units is as follows:

	Sp. gr.	*B.Th.U. per lb.*	*B.Th.U. per gal.*
Persian fuel oil	0·895	19,060	170,500
Trinidad fuel oil	0·955	18,810	179,600
Low-temperature tar, topped	1·065	16,930	180,300
Low-temperature tar oil	1·014	16,780	170,150
Low-temperature tar, neutral oil	0·966	17,830	172,250

This shows that the tar products do not compare unfavourably with petroleum oils as regards storage capacity on a thermal basis.

Diesel Engine Fuel

Topped low-temperature tar cannot be used as a Diesel fuel, but the tar oil boiling between 200 and 360° C. is more promising. It does not conform to existing specifications for petroleum oils in that its specific gravity and ignition temperature are high, but its viscosity, flash-point, distillation range, sulphur, water, and ash contents are all satisfactory.

Experimental work on a Mirlees Diesel in 1927 [2] indicated some difficulty in starting, but showed that with a warm jacket the oils gave as good performance as a shale fuel oil. These tar oils were distilled from tars produced in an internally heated retort. T. F. Hurley and M. A Matthews [7, 1931] record experiments with a similar oil produced from tar from an externally heated retort; they find, however, that with several types of engine, four-stroke, two-stroke, solid and air injection, the performance was not so satisfactory. Difficulties were encountered with starting and harsh running under full load, but when running was satisfactory the carbon deposit was not great, and the valves and ports remained clear. In the Admiralty experiments [3, 1933] on a slow-running Diesel of the submarine type, satisfactory performance was obtained at full power with normal blast-pressure and with a reasonable fuel consumption after slight modifications had been made to the jets to give finer atomization.

It seems, therefore, that tar oils can be made to work satisfactorily in slow-running Diesels, but as the speed increases they give trouble owing to difficulty in ignition. This has been confirmed by indicator cards which show a marked ignition lag in comparison with shale oil. The obvious reason for this is the high proportion of aromatic hydrocarbons in the oil and a high spontaneous ignition temperature in the neighbourhood of 500° C. The difficulty can be overcome in some engines by finer atomization but, without some means of reducing the ignition lag, the oils are unsuitable for the high-speed Diesel. Such remedies as suggest themselves are:

(i) Pilot ignition, i.e. pre-charging of a small amount of easily ignited fuel.
(ii) The use of a starting fuel, changing over when the engine is hot.
(iii) Blending with fuels of low-ignition temperature.
(iv) The use of 'dopes' such as ethyl nitrate to reduce ignition temperature and ignition lag.

Expedients (i) and (ii) are not practicable, and (iii) could not have more than a limited application. The last expedient is attractive, but the dopes so far discovered are too expensive, increasing the cost of the oil by as much as one penny per gallon. In the R.A.E. (Farnborough) method of test it has been shown that creosote, with an ignition temperature of 480° C., has a delay time of 2 sec. at 500° C. in comparison with a fuel-oil figure of 0·2 sec. The addition of 2% of ethyl nitrate to this fuel oil reduced its delay time to less than 0·1 sec. The effect of these dopes on low-temperature tar oils has not yet been examined, but it is possible that this method of attack of the problem may be helpful.

B. Broche, K. Ehrmann, and W. Scheer [1, 1932] have examined high-temperature tar oils having spontaneous ignition temperatures of from 440 to 470° C., and have been able to decrease the temperature by as much as 200° C. with metallic catalysts. This result has led them to suggest a design of engine in which a metallic catalyst is arranged in a pre-mixing chamber. The idea does not seem to have been followed up, but it is possible that some improvement in engine design may overcome present difficulties.

The neutral oil obtained by removing the tar acids from low-temperature tar oil is appreciably less unsatisfactory than the oil itself. The ignition temperature of neutral oil is about 50° C. lower than that of the tar oil from which it is prepared. This finding refers to tars from bituminous coal, since the German Mineral Oil Research Association report that the tar oil from brown coal is a good Diesel fuel despite the fact that it contains 35–40% of tar acids. On account of its low calorific value consumption is rather high. A more recent paper on tar as a fuel is that of J. G. King and C. M. Cawley [8, 1936].

Lubricating Oils

It has been suggested that a really primary low-temperature tar should contain oils of a lubricating character, but research has shown that, though fairly viscous oils are obtainable by refining and vacuum-distillation, these are unstable and break down rapidly to coke under working conditions. This is confirmed in Germany by the findings of the German Mineral Oil Research Association (1934). The hydrogenation of tar or tar oils has also proved a barren source as yet. Lubricating oils can, however, be produced from the low-boiling oils or spirit by polymerizing the unsaturated hydrocarbons with aluminium chloride. If a spirit be refluxed in the presence of this substance and the oil distilled *in vacuo*, a series of lubricating bases are obtainable whose viscosities vary from a light spindle oil to a heavy engine oil.

Fuel Research experiments [10, 1934] have shown that the combined oils amount to 8 per cent. by weight of the spirit treated and that they are all clear yellow oils of good odour. Compared with petroleum oils these products had poor viscosity indices, but were satisfactory lubricants when not subjected to high temperatures.

REFERENCES

1. Broche, B., Ehrmann, K., and Scheer, W. *Glückauf*, **68**, 978 (1932).
2. Brown, J. S. *J. Royal Technical College*, **4**, 76 (1927).
3. Dunlop, S. H. *Trans. Inst. Eng. Shipbuilders, Scotland* (7 Nov. 1933).
4. Fuel Research Survey Paper, 18 (1931).
5. Fuel Research Technical Paper, 32 (1931).
6. Fuel Research Technical Paper, 34 (1931).
7. Hurley, T. F., and Matthews, M. A. *J.S.C.I.* **50**, 584 (1931).
8. King, J. G., and Cawley, C. M. *J.I.P.T.* **22**, 595 (1936).
9. Morgan, G. T. *J.S.C.I.* **51**, 67T (1932).
10. *Report of Director of Fuel Research, Year ending March 31, 1934*, p. 94.

HIGH-TEMPERATURE COAL TARS

By **W. G. ADAM, B.A., F.I.C., M.I.Chem.E.**

Superintendent, By-products Works, The Gas Light and Coke Company, London

COAL tar, being a by-product of the gas- and coke-making industries, depends for its properties upon the type of carbonizing plant employed, the nature of the coal, and the conditions under which it is carbonized. An endeavour will be made to show, as completely as possible within the scope of such a short article, the effect of these varying conditions upon the properties, composition, and utilization of the resulting tars and their products. Before commencing to discuss such variations in the nature of tars, a brief outline of the purely physical aspects of tar would be appropriate. All high-temperature tars are colloidal systems, the stability of which depends upon their method of production and subsequent treatment. They consist essentially of finely dispersed particles, usually termed 'free carbon', in an oily medium, the stability of the system being attributed to the protective influence of the tar resins upon the colloidal particles. Adam and Sach [3, 1929] consider that the actual suspended matter in a tar corresponds to the fraction of the tar insoluble in pyridine, to which they attach the symbol C_1. If, however, the tar is dissolved in benzene or toluene instead of in pyridine, a further fraction, called by these workers C_2, is precipitated so that the so-called 'Free Carbon' of tar, i.e. the material insoluble in benzene or toluene, consists of C_1+C_2. C_1 is a dull black powder little affected by heat, but C_2 is more resinous in character and intumesces under the influence of heat. If the benzene-soluble portion of tar is treated with a considerable excess of petroleum ether, a further class of resin is precipitated which varies slightly in colour according to the nature of the tar, but is usually light to reddish-brown. This technique has been adopted by Morgan and Mitchell [12, 1935] in their research upon high-temperature tar at the Chemical Research Laboratory, and they further treat this resin insoluble in petroleum ether with diethyl ether, whereby they subdivide it into soluble and insoluble portions, which they label C_4 and C_3 respectively. They report also that the fractions C_2, C_3, and C_4, when dissolved in anthracene oil to the same concentration, produce tars of widely different viscosities. C_3 tar is only one-twentieth as viscous as C_2 tar, whilst C_4 tar is approximately half as viscous as C_3 tar. It will be readily seen, therefore, that the viscosity of tar depends to a great extent upon the proportions of these different fractions present.

Taking the compounds insoluble in petroleum ether as one fraction, we can therefore, as far as present knowledge allows, consider tar as consisting of four groups of substances, viz. the suspended or colloidal particles insoluble in such solvents as pyridine, a resinous fraction soluble in pyridine and insoluble in benzene, which may be present either in true solution in the oils or as an ultra-colloid, and thirdly what might be described as the tar resins, i.e. the compounds soluble in pyridine and benzene, but insoluble in petroleum ether, and which are believed to be in a state of true solution in the oils or the fourth group of substances, otherwise known as the fraction soluble in petroleum ether. There is little doubt that tar derives its adhesive qualities from these solutions of resins in oils, as a simple experiment will show, but the source of its undoubted binding power, e.g. in road construction, is not so readily defined. In view of its marked influence upon viscosity the fraction C_2 may be of importance, but there is scarcely any published data available from which to decide.

Tar resins, when heated, become plastic and begin to decompose as the temperature is raised to approximately 140° C. For this reason, resolution by solvents is the best method of studying the constitution of tar [20, 1929], provided suitable low-boiling liquids are employed. The recovery of the solvent by vacuum distillation will often prevent the use of too high a temperature. It is the generally accepted view that the tar resins are derived in the first instance from the oils and that the resinous constituents of the benzene-insoluble fraction (C_2) are merely a higher form of the petroleum-insoluble resins. Marcusson [19, 1919] investigated the formation and structure of tar resins, and suggested they originated from the oxidation or polymerization of unsaturated hydrocarbons present in the heavy tar oil and contained oxygen in the nucleus. Asphaltenes and petroleum resins are likewise formed from heavy mineral oils, and Marcusson suggested that the tar resins might be known as 'aromatic asphalt', a name which would certainly indicate their character. Morgan and Mitchell [12, 1935] have shown that tar absorbs oxygen with the formation of a benzene-insoluble resin, thus supporting Marcusson's ideas of resin formation and also his suggestion that the lower tar resins absorb oxygen and are converted to the higher type. The suggestion has also been made by Adam and Sach [3, 1929] that tar resins are also formed from the alkali-soluble constituents of tar. The changes occurring in tar on exposure to the atmosphere will be dealt with later in this article, when it will be seen that in a tar used, say, for road purposes the changes due to exposure occur very slowly indeed.

The ultimate composition of the 'free carbon' (C_1+C_2) of tar has been determined by several workers, among them being Donath and Asriel [6, 1903], who found C 89·2, H 2·3, N 3·7, O 7·13%, and Adam and Sach [3, 1929], who reported C 90, H 2·8%, whilst similar results were obtained by Hubbard and Reeve [22, 1911], and Weiss [28, 1914]. Marcusson [18, 1930] examined the 'free carbon' of coal tar obtained from vertical and horizontal retorts, and resolved it into groups consisting of oxy-acids, pyridine-soluble resins, pyridine-insoluble resins, and partly coked material, and suggested a method for determining the latter.

High-temperature tars are usually given names denoting their origin, so that we have horizontal-retort tar, vertical-retort tar, and coke-oven tar, the term vertical-retort tar embracing tars produced in both intermittent and continuous vertical retorts. The tar produced during the carbonization of coal at low temperatures is usually referred to as low-temperature tar. The amount of coal carbonized annually in gas works in Great Britain is of the order of 17–18 million tons, of which about 50–5% is treated in horizontal retorts and the remainder in vertical retorts, with the exception of a small amount treated in inclined retorts and coke ovens. Approximately 16–17 million tons of coal are carbonized annually in coke ovens in Great Britain. The quantity of tar produced in gas works is between 210 and 215 million gallons per annum, and in coke ovens about 130–40 million gallons. Tables giving the estimated world production of tar both collectively and according to the country of origin will be found at the end of this article. According to Hunter [15, 1933] the yields of tar per ton of coal carbonized in the main carbonizing units are as follows:

Type of plant	*Tar made. Gal. per ton of coal*
Continuous verticals . . .	10·1
Intermittent verticals . . .	11·7
Coke ovens	9·02
Horizontals	9·42

TABLE I

	Horizontal retorts		*Coke ovens*		*Intermittent vertical retorts*	*Continuous vertical retorts*		*Low-temperature carbonization*
	High temps. Light charges	*High temps. Full charges*	*Rapid narrow ovens*	*Slow wide ovens*		*A*	*B*	
Specific gravity of well-settled tar at 15·5° C.	1·19	1·16	1·17	1·17	1·15	1·11	1·07	1·03
Distillation % by wt. on dry tar—								
To 200° C.	3	5	3	2	3	5	5	9
200–230° C.	6	7	6	3	8	11	10	16
230–270° C.	10	11	12	7	12	14	12	13
270–300° C.	4	4·5	5	6	7	7	7	9
300°-medium pitch . . .	10	12·5	9	11	8	12	14	18
Medium pitch	67	60	65	71	62	51	52	35
Crude tar acids in 200–270° C. fraction—								
% by vol. of fraction . . .	12	20–5	14	20–5	20–30	20–50	35–40	45
% by vol. on dry tar . . .	1½–2	4–5	3	4–5	5–6	6–12	8–10	17
Naphthalene in 200–270° C. fraction (road tar method) % by weight on dry tar	7	4	7	4–6	0–1	trace	nil	nil
'*Free carbon*', % by weight . .	23	15	6	15	3	4	3	1
Specific gravity of distillates at 15·5° C.—								
To 200° C.	0·950	0·930	0·950	0·950	0·900	0·910	0·900	0·860
200–230° C.	1·010	1·000	1·015	1·005	0·980	0·960	0·950	0·940
230–270° C.	1·040	1·030	1·048	1·035	1·020	0·995	0·990	0·980
270–300° C.	1·062	1·055	1·070	1·060	1·044	1·015	1·002	1·000
300–350° C.	1·102	1·098	1·110	1·098	1·086	1·045	1·035	1·030

High-temperature carbonization is generally carried out at retort temperatures in the neighbourhood of 1,100° C. as distinct from the temperatures around 600° C. usually adopted in low-temperature processes.

The conditions inside the various retorts and ovens are naturally different, and these differences are reflected in the properties and constitution of the tars produced. Table I is reproduced from *Technical Data on Fuel*, edited by H. M. Spiers, and illustrates typical properties of tars belonging to the various groups. The figures given are based upon analyses carried out in the Woodall-Duckham laboratories, but it must be borne in mind that these are 'typical compositions' and that fairly wide variations can occur in the compositions of tars belonging to the same group. It is possible, nevertheless, to draw a number of general conclusions regarding the physical and chemical properties of tars produced under different conditions. It will be seen that horizontal-retort and coke-oven tars have higher specific gravities than the vertical-retort tars, a difference which is marked also in their corresponding distillates, whilst it is interesting to make a comparison with low-temperature tar, which is in a class by itself much lower down the scale. The differences between the tars become more pronounced if we compare their 'free carbon', naphthalene, and phenol contents. The 'free carbon' of horizontal-retort tar is much greater in amount than that of vertical-retort tar, whilst coke-oven tar holds an intermediate position with a tendency towards low figures in general practice. Horizontal-retort and coke-oven tars both contain a reasonable percentage of naphthalene, which substance, however, is almost entirely absent from vertical-retort tar, and more so from low-temperature tar. With regard to the phenol content, the position is reversed and vertical-retort tar contains considerably more of this constituent than either horizontal-retort or coke-oven tar, and, following the usual sequence, low-temperature tar contains even more than the vertical-retort tar. The yield of pitch of medium hardness is greater on distillation of horizontal-retort and coke-oven tars than with vertical-retort tars, and more will be said later regarding the pitch recovered from low-temperature tar. Apart from differences in percentage composition the tars vary as regards the composition of the constituent groups, e.g. the neutral oil fraction of vertical-retort tar contains a considerable proportion of paraffinoid and unsaturated substances, whilst the corresponding fraction of horizontal-retort and coke-oven tars are practically free from these compounds. Low-temperature tar is rich in paraffins and unsaturated hydrocarbons. Variations in the composition of other groups, e.g. the phenols, will be discussed under their separate headings.

The tar produced in any given type of retort will vary in constitution according to the details of operation of that retort, e.g. regarding size of the retort, the amount of the charge, upon which depends the volume of free space, and the temperature of the combustion chamber surrounding the retort. This question has been dealt with by Hollings [14, 1926] and Fieldner and Davis [8], and it appears that the size of the retort is of importance because it governs the carbonizing period and consequently the period during which the vapours are in contact with the hot coke whilst the velocity of the gas is low, whilst an increase in the free space causes cracking of the tar, resulting in an increase in the specific gravity and in the free carbon, naphthalene, anthracene, and pitch contents, and a decrease in phenols, neutral oils, and olefines. The effect of variations in the mean carbonizing temperature already quoted for high-temperature processes will be to bring about, on a much smaller scale, differences in the tar similar to those existing between high- and low-temperature tars. Increases in the carbonizing temperature will tend to bring about increases in the 'free carbon' content of the tar, and, as will be shown later, there is an upper limit to 'free carbon' beyond which it is inadvisable to go, so that if the tar is to be marketed, the temperature of carbonization must be maintained within a suitable range. The lower limit of 'free carbon' is likewise controlled, but the requirements of gas-making usually ensure compliance of the tar in this respect. In addition, the nature of the coal carbonized will have some bearing upon the properties of the tar, but as regards English gas coals, more upon the percentage composition than upon the nature of the tar. To quote Warnes [25, 1923]: 'Practical working has shown that North Country coal yields a tar which on distillation gives a fairly low percentage of light oils and a rather high yield of creosote, naphthalene, and anthracene, while tar produced from Midland and Yorkshire coals yields on distillation rather more light oils and less creosote, naphthalene, and anthracene; that is if comparative methods of carbonisation and temperatures are employed.'

Although opinion is divided upon the actual reactions governing the formation of high-temperature tar compounds, it is generally conceded that they are formed principally as a result of secondary reactions upon the low-temperature tar first formed as the coal is gradually heated. Contrary to earlier opinions on the subject, it has been realized that aromatic compounds are not only present in low-temperature tar, but represent one of the main constituents. As the aromatic compounds appear to change little as a class on pyrolysis, it seems probable that those present in low-temperature tar are the parent substances of those in high-temperature tar. The suggestion has also been made that the lower boiling aromatic constituents of high-temperature tar may be formed by the reduction, dealkylation, or dehydrogenation of phenols and naphthenes, whilst the decomposition of the naphthene, paraffin, and unsaturated hydrocarbons of low-temperature tar into higher olefines, and the condensation of the latter to aromatics, has also been proposed. The phenols of high-temperature tar might possibly result from the dealkylation or partial hydrogenation of the more complex phenols in low-temperature tar, but as such a reaction would require rather close control, it seems more probable that the phenols survive as a group in a more stable form. The mechanism of coal-tar formation will doubtless remain rather obscure owing to the difficulty there will always be in reproducing the correct conditions for the study of the pyrolysis of the various classes of compound. The literature on the subject has been well reviewed by Kester and Pohle [24, 1932] in their study of the composition of the fractions of primary and high-temperature tar.

The greater part of the high-temperature tar produced nowadays in Great Britain is distilled. Until recent years the increasing use of tar for road purposes, coupled with the development of new processes of distillation, tended to encourage the decentralization of distillation units, but at the present time, owing to the exigencies of modern specifications and the consequent necessity for expert technical supervision, the position is more or less reversed. A number of the larger manufacturers of gas and coke still refine their own tar, but there have arisen throughout the country numerous district organizations treating the tar produced in certain areas at a central distillery. This system has resulted in a high level being maintained in all parts of the country in the quality of the tar used for road purposes, and has done much to popularize its use.

The types of distillation plant available to the tar distiller may be classified as follows:

1. Intermittent pot or longitudinal stills.
2. Continuous stills, usually consisting of several specially designed stills in series.
3. Continuous pipe or coil stills.

Pot stills, which are usually constructed of wrought iron or mild steel, vary in capacity between 15 and 40 tons, and the vertical type are fitted with concave bottoms to present a greater heating surface and prevent buckling at high temperatures. These stills, however, are rarely used as a single unit, but generally form part of the double-still system, which consists of a pot still working in conjunction with some form of economizer whereby the crude tar for the next charge is gradually heated by means of a coil carrying the vapours from the fire still. By this means the aqueous liquor, which may be present in the crude tar to the extent of 3–8%, is slowly distilled off along with a portion of the light distillate, thus resulting in a considerable saving of time, as the tar passing forward to the fire still is free from water and can be distilled quickly without fear of frothing. Pot stills are so fitted that free steam can be admitted, particularly during the latter part of a distillation to pitch, in order to prevent cracking of the products.

It was but a short step from the intermittent to the continuous still of which the Hird system is typical. Briefly, this consists of a number of flat-bottomed stills in series, the tar passing in a baffled stream over the bottom of each still in succession. The number of stills in series is usually three or four, depending upon the extent to which the distillation is to be carried, the heating being by means of flue gases passing through internal tubes. Heat exchange is arranged between the incoming wet tar and the tar vapours and hot tar or pitch leaving the stills, thus ensuring the preliminary dehydration of the crude tar before its entry into the still proper. The temperatures in the separate stills comprising the series are so adjusted that the tar is divided into the customary fractions during its passage through the plant. The advantages offered by the continuous process are as follows: (*a*) Ready control of rate of distillation and range of distillates; (*b*) considerable reduction in labour and fuel costs; (*c*) relatively higher output per unit of capital expenditure; (*d*) complete absence of priming or frothing. Another type of continuous tar-distillation plant is the T.I.C. plant. In this process the previously dehydrated tar is distilled by passing it in a thin film over a low-melting alloy heated to a temperature dependent upon the range of product required, the vapours being fractionally condensed to give suitable oils. After traversing the molten metal, the residual tar may be steam distilled, according to the circumstances. In several works ordinary pot stills have been arranged to work continuously by placing at suitable heights so that the tar runs from the first to the last, being controlled by suitable overflow apparatus.

In 1907 Wilton obtained a patent for a tar-dehydration plant in which the tar is passed continuously through a cast-iron coil, in which it is heated to a temperature of 170° C., while being maintained under a pressure of 40/60 lb. per sq. in. From the exit of the coil the tar passes to a vessel in which the superimposed pressure is reduced to that of the atmosphere, and volatilization of the water and light oils now takes place. The sudden 'flashing off' of the vapours at the point of expansion eliminates the frothing trouble, and the partially distilled tar may now be completely distilled to pitch in a pot still without difficulty. The modern practice, however, as applied to the production of road tar, is to discard the pot still and continue the distillation in an additional coil working on the same principle as the first, but heated to a higher temperature, e.g. 270° C., for the production of a thick base tar. The Lennard plant distils tar completely to oils and pitch under somewhat similar conditions, the separation of the oil-vapours into the required fractions being obtained by fractional condensation. One advantage offered by the coil system is safety, because of the relatively small amount of tar present in the plant at any time, whilst on account of the short period during which the tar is at the distillation temperature cracking is reduced almost to a minimum, so that higher yields of oil are obtained.

This question of cracking had a considerable influence upon the design of modern pipe and coil stills for the distillation of tar. It was known that after a distillation of tar to pitch in, for example, a pot still, the 'free carbon' content of the pitch was greater than would have been expected from concentration alone. Adam and Sach [3, 1929] in their study of 'free carbon' formation in coal tars and pitches point out that unless serious local overheating of the tar occurs, the total material insoluble in pyridine (C_1) remains reasonably constant, so that any increase in the total 'free carbon' (C_1+C_2) present is due to formation of C_2 during the distillation. This occurs more readily with vertical-retort and coke-oven tars than with horizontal-retort tar, and tends to reduce the yield of oil and, if excessive, to affect adversely the quality of the pitch. The above authors suggested the observance of the following points in the design of a tar-distillation unit: (*a*) Minimum final temperature in the tar obtained by employing a high vacuum, or by the use of free steam. The latter method also assists by improving the agitation of the tar, thus reducing local overheating. For distillation to briquetting pitch, final tar temperatures should not exceed 280–300° C. (*b*) The time of exposure of the tar to the maximum temperatures should be reduced to a minimum, a result obtained by continuous distillation methods, particularly in a coil-type unit. In addition they give the results of a distillation carried out according to the process patented by the Gas Light and Coke Company, [Adam and Potter 10, 1927], which embodies the above principles. The results show that the ratio

$$\frac{\text{Total insoluble in pitch}}{\text{Total insoluble in tar}}$$

was maintained at substantially unity for both C_1 and C_1+C_2, i.e. the material insoluble in pyridine and benzene respectively. This process follows the coil system and provides facilities for fractionating the vapours and for steam distillation of the soft pitch leaving the coils, so that a pitch of any desired softening-point can be obtained. The description just given would apply in a general manner to several other pipe or coil stills at present in use, as the governing principles are the same, and it is only in detail that differences occur. The employment of vacuum is a feature of some modern units, and it assists in maintaining reasonably low temperatures. Pipe stills are used extensively in America and on the Continent, and it is claimed for some of them that such close fractionation is possible that redistillation of the oils to obtain, for example, a naphthalene fraction is rendered unnecessary. The new Wilton coil plant [29, 1933], recently introduced, deserves mention for some of its features, perhaps the most interesting being the introduction of crude tar after the heating coil, when it is dehydrated and partially distilled by admixture with a portion of the hot pitch leaving the vapour box, the mixed residue being recirculated through the coil. The rate of addition of crude tar to the pitch is thermostatically controlled by the temperature of the latter.

Brief mention must be made in passing of yet another type of process for tar distillation—one that can only be used in conjunction with a carbonizing plant. By this is meant a process such as that covered by the Barrett Company of America in a long series of patents, and in which the tar is distilled by being brought into direct contact with raw hot coke-oven gas, the pitch being separated and the gases cooled to recover the oils either in bulk or by fractional condensation. Another process worked on similar lines is that developed and patented in England by Cooke and adapted by him to both coke-oven and gas-works practice. It is claimed for this type of process that there is little or no fuel expense, a short time factor, and a relatively high yield of distillate.

In dealing with tar distillation the author has endeavoured to discuss principles with reference to typical working processes, and for further information relating to the latter and many similar processes reference should be made to recent literature upon the subject [7, 1935; 26, 1930; 27, 1932].

The selection of a particular process will be governed by such factors as capital expenditure, ground available, local markets, and more particularly by the throughput of tar required; and each case must be decided on its merits. The total quantity of gas-works and coke-oven tar distilled in Great Britain in 1934 was 330 million gallons, of which 214 million gallons were from gas works and 116 million gallons from coke ovens. Probably 50–60% of this quantity was distilled to pitch, the remainder being used in the production of road tar and other refined tars. Road tar and other special grades of tar are generally prepared on the 'cut-back' principle, with the exception of the high-viscosity tars required for hot-process tarmacadam or tar concrete. The tar is distilled until a product is obtained considerably higher in viscosity than is required for the finished tar, and this is fluxed with tar distillate or a combination of distillates until the correct consistency is attained. A full understanding of the factors controlling the quality of a road tar, such as the extent of the distillation to base tar, and the nature and proportion of the fluxing oils used, is only acquired by research and experience, and it cannot be too strongly emphasized that expert supervision is necessary to produce tars such as are marketed to-day, capable of withstanding all conditions of weather and traffic. British Standard Specifications no. 76–1930 and no. 76–Part 2–1931, cover Tars nos. 1, 2, and 3 for road purposes such as surface dressing and tarmacadam work, but it is pointed out that surveyors may at their discretion specify higher viscosities, and the tendency nowadays is towards the use of much higher viscosity tar for surface dressing than is suggested by the specification for no. 1 Tar. This will no doubt result in a fairly early revision of the specifications which were prepared in the first instance for the British Standards Institution by the British Road Tar Association, a body which has done much to advance the use of tar for roads in Great Britain.

The process for the tar-spraying of roads has changed considerably both as regards materials and technique since the early days when crude tar was often employed. Although there may be earlier mention of the use of tar in road construction, the experiments carried out by Dr. Guglielmenetti on the Riviera in 1901 represent the first systematic work upon the subject of surface treatment. The competition organized in 1907 by the Roads Improvement Association to determine 'the best form of tar or preparation of tar suitable for road purposes' did much to improve the quality of road tar. Its success brought about an increasing demand for good-quality road tar, with the result that the Road Board, in 1911, issued its first specifications for tars for the surface dressing of roads and for tarmacadam. These were subsequently revised and later on merged into the British Standard Specifications previously mentioned. The spraying of roads with tar nowadays follows well-defined rules, which are briefly as follows: The surface of the road should be swept free from dust and any irregularities made good, the tar then being applied evenly to the dry road at a temperature between 200 and 240° F., depending upon its viscosity. The area covered by a given amount of tar is adjusted to suit the requirements, as the nature and texture of the surface will vary, whilst some roads will have been previously tarred and others not, so that in practice the figure varies between 4 and 8 sq. yds. of road surface for each gallon of tar used. Following the tar-spraying, the road must be dressed with clean, hard, stone chippings or shingle of ⅜-in. to ½-in. gauge, followed by a light rolling, this latter treatment being most important, because if it is omitted there will be a tendency for the stone to be swept to the side of the road by fast traffic, exposing bare patches of tar. If, however, a tar of suitable viscosity is properly laid on the above-mentioned lines, an excellent non-skid surface should result which will maintain its character under all conditions. By 'suitable viscosity' is meant the viscosity chosen with regard to the condition of the existing surface, the season of the year, and the size of the gritting material. It is characteristic of tar that, on exposure to the atmosphere, it forms a surface possessing valuable anti-skid properties quite apart from those attributable to the stone dressing. Tar after two years' exposure to the atmosphere still contains more than 50% of oils soluble in petroleum ether, and remains plastic. A certain amount of resinification occurs as evidenced by an increase in the 'free carbon' and a much greater increase in viscosity than can be attributed to loss of oils by evaporation, but the tar still retains its adhesiveness and binding power. Furthermore, excellent non-skid roads can be constructed with high-temperature tar irrespective of its source, i.e. whether it is derived from horizontal retorts, vertical retorts, or coke ovens, provided due regard is paid to all the points mentioned. The demand nowadays is for 'long life' in surface dressings, and as a result of research the tar distiller is in the position of being able to produce the 'high durability' tars required. If required also, a tar can be supplied containing little or no material of a toxic nature, extractable by water, so that it can be used in the vicinity of lakes and streams and minimize the danger of giving rise to pollution of the latter. A process for the production of such a tar has been patented by the Gas Light and Coke Company, [Adam, Murdoch, and Potter 9, 1932], and consists of blending a soft pitch which has been maintained at a temperature of 300–315° C. for a period of 12–24 hours, with a creosote oil from which the phenols, tar bases, and crystallizable naphthalene have been removed. An important feature of the invention is the heat treatment of the soft pitch whereby any phenols present almost disappear with the probable formation of resinous compounds (vide Adam and Sach [3, 1929]).

It should be mentioned also that the old hand-spraying equipment has been largely superseded by motor or steam-propelled vehicles fitted with heat-insulated tanks and spraying devices, which are capable of laying an even carpet of tar of predetermined thickness, and varying in width according to requirements, the maximum being between 7 and 13 ft., according to the type of vehicle. These tank lorries can be loaded with hot tar at the plant, and the insulation of the tank permits transport to a considerable distance before use, whilst in addition some of these vehicles are fitted with apparatus for heating the tar in transit, thus increasing their range. They are often used in conjunction with mechanical gritting machines, the advantages of the whole system being obvious. A more recent development in the surface treatment of roads has been the introduction of thin wearing carpets which are being used in cases where the state of the existing surface demands such treatment, and where it is considered surface-spraying would hardly suffice. These carpets, which are generally of 1-in. thickness, consist of carefully proportioned mixtures of tar and fine-graded stone or gravel, and their future will be watched with interest by all concerned.

Tarmacadam work may be any of three types—three-coat, two-coat, or single-coat—and of the three, single-coat work is becoming of increasing importance, whilst three-coat work is less frequently seen. Two-coat work, as the name implies, consists of a base coat of relatively coarse material and a wearing course of much finer texture, the consolidated thickness of the base coat being approximately three-quarters that of the whole, which varies from 3 to 4 in. Single-coat tarmacadam is usually laid to a consolidated thickness up to 3 in. and, in a similar manner to two-coat work, is given a seal-coat of tar and chippings after an interval to allow consolidation by traffic. The stone used in both types ranges in size from 2 in. to ⅛ in., and in addition a small amount of filler is employed. The number of gallons of tar added per ton of aggregate varies from 6 to 9 for base and single-coat mixings, and from 8 to 14 in the wearing course, according to the grading of the stone. The tar used conforms to the British Standard Specifications for Tar no. 2 or Tar no. 3. More recently there has been introduced a form of single-coat tarmacadam known as hot-process tarmacadam or tar concrete. As the name implies, the object has been to obtain a very dense product, i.e. one low in voids, and for this reason the mixture contains a higher percentage of small material. The grading of the stone is from 1 in. down to ⅛ in., but the aggregate may contain as much as 35–40% of material smaller than ⅛ in., one-half of which probably passes an 80-mesh sieve. The binder is a soft pitch testing 10–25 sec. at 60° C. by the B.S.I. efflux tar viscometer, the amount used varying between 12 and 15 gal. per ton of total aggregate. A seal-coat of tar and chippings may be applied at a suitable interval after the tar concrete has been laid. This type of material can also be laid on the two-coat principle, the base coat being of much coarser texture than the wearing course, but as a rule the two-coat system is only employed in cases where the consolidated thickness of the tar concrete is required to be greater than 3 in., which is the maximum figure adopted for the single-coat type. Tar concrete has shown itself particularly adaptable to roads carrying large volumes of fast-moving traffic, as evidenced by the success attending its use on the Kingston By-pass in this country, and on numerous roads in Germany.

There are a number of rules which should be observed in the manufacture and laying of tarmacadam, and they are briefly as follows: (*a*) A grade of tar should be selected most suitable for the type of aggregate employed; (*b*) the aggregate should be dry; (*c*) both binder and aggregate should be separately and carefully heated to a temperature within the range specified for the particular type of material being manufactured; (*d*) avoidance of the use of too little tar; (*e*) the commencement of rolling should be governed by the texture and pliability of the material, that is to say, it should not be rolled whilst too hot or too cold. Rolling should not be continued after the correct degree of compression has been attained. (*f*) The materials should be protected from inclement weather during transit; (*g*) the grading of the aggregate should be chosen with particular regard to the requirements demanded of the finished macadam. The observance of these rules will ensure satisfactory service, provided that a suitable foundation is available, as control of the manufacture of the macadam cannot overcome the handicap of insecure foundations.

Apart from tar itself, considerable employment has been found in road construction for tar bitumen mixtures and tar emulsions. By the former are usually understood mixtures of refined tar and petroleum bitumen, the latter substance seldom forming more than 20-5% of the whole. It is the belief of those who favour their use that these mixtures combine the advantages of both constituents. Their manufacture calls for considerable care, both in the selection of materials and the method of mixing, as the maximum amount of a given bitumen which it is permissible to add to a tar depends largely upon the nature and properties of the latter. Should an attempt be made to add more than this quantity, the internal structure of the mixture is affected and coagulation occurs with the formation of lumps of resinous material, thus destroying the homogeneity which is one of the salient features of tar. If required, the petroleum bitumen can be replaced by natural asphalt, the amount added being inversely proportional to the percentage of bitumen in the latter. The use of tar emulsions is increasing, and British Standard Specification no. 618–1935 dealing with these products has been published. Their general characteristics and uses are identical with those of the corresponding bitumen emulsions. Tar emulsions, however, must not be confused with cold tars, which are a special grade of refined tars suitable for use at ordinary temperatures, and consequently in favour for patching work and other small-scale operations. They consist essentially of refined tar thinned down to a suitable degree with a readily volatile solvent, which, after the laying of the tar, quickly evaporates, leaving a tar of normal consistency. The use of these products has developed considerably in Germany and America.

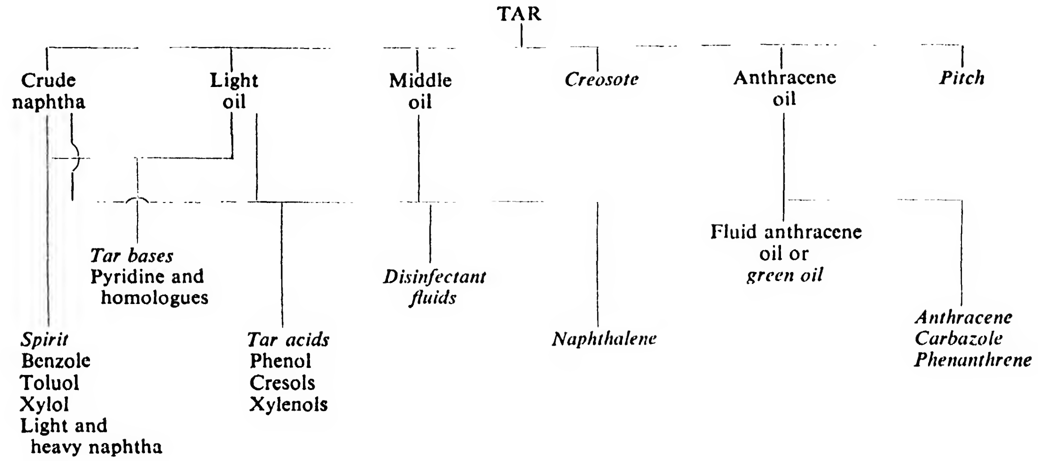
A summary of the use of tar in road construction would not be complete without mention of the work of Dr. F. J. Nellensteyn, chief of the Government Road Laboratory in Holland, who has advanced some interesting theories upon the structure of tar and particularly stresses the importance of the size and degree of protection of the particles of 'free carbon'. Further, he has suggested a method [21, 1933] for determining the so-called 'micron number', i.e. the number of particles of a certain average size present in a mm.^{3} of tar, which involves diluting the tar 100 times with nitrobenzene, removing the coarse particles by filtration through a certain class of filter-paper, and counting the particles in the filtrate with the aid of a Thoma haemocytometer. The 'unfiltered' micron number is also determined by diluting the original solution in nitrobenzene still further and counting the particles before filtration. Nellensteyn fixed minimum figures for the 'micron numbers' he considered essential in a good road tar, and these were 10–15 million per mm.^{3} (filtered) and 50–100 million per mm.^{3} (unfiltered), according to the purpose for which the tar was required. It is to be feared, however, that the test will not give reproducible results in the hands of different workers, and for this reason alone, apart from the merits or otherwise of Dr. Nellensteyn's theories, it is doubtful whether the test will command much attention in future as a means of examining commercial samples, although it may be of use to the research worker.

From time to time, also, processes have been patented for the production of tars having, it was claimed, enhanced properties in various connexions. These processes usually involved either some form of chemical treatment of the tar or the incorporation in the latter of a given substance or group of substances. Of the many tars so produced, however, only a few seem to have survived the test of experience.

Apart from its use in road construction, refined tar finds extensive application as a paint, preservative, and general weather-proofing agent for metal and wooden structures, as well as for fabrics such as tarpaulins, roofing felts, &c. A typical modern development has been the adoption of a specially prepared tar as a sealing medium in waterless gasholders, for which purpose it seems particularly well suited. The amount of refined tar used at present on road construction in Great Britain is of the order of 120 million gallons per annum. (See also tables at the end of this article.)

When considering the various products normally obtained on a commercial scale at a tar-distillation works, it is important to remember that creosote, refined tar, and pitch together constitute 90% or more of the total quantity produced, the term creosote being used in its broadest sense.

The chart on p. 3124 details on a flow diagram the progress of a complete distillation of tar to pitch, together with the products available commercially at present either as separate compounds or groups of compounds, and obtainable by further treatment of the primary products of distillation. Road tar and other refined tars find no mention on this chart, as their method of production and uses have been adequately covered. A quantity of ammoniacal water is recovered along with the crude naphtha, and is separated and sent for purification with the main bulk of ammoniacal liquor from the gas works. The crude naphtha may contain up to 60% of light spirit, the remainder consisting largely of naphthalene, together with a small percentage of phenols and bases. These latter two groups of substances are removed by washing the oil with 10% NaOH solution and 25% H_2SO_4 respectively. The washed oil is then fractionated to recover the light spirit, which passes to the benzole plant for purification along with the remainder of the crude spirit recovered direct from the gas by the wash oil or active carbon process. The spirit is either submitted to the acid-washing process and then fractionated, or given a preliminary wash with dilute NaOH and dilute H_2SO_4, fractionated, and treated by the inhibitor process [13, 1933], which consists in adding to the freshly distilled spirit an extremely small percentage of a given compound possessing the property of inhibiting gum formation. The crude spirit is often given a preliminary distillation to separate it into appropriate fractions before it undergoes either of the above treatments. The selection of a particular process of purification is governed by the requirements demanded of the finished product. A certain amount of carbon disulphide and other low-boiling compounds is obtained in the early stages of the distillation, but otherwise the finished products comprise pure benzene, pure toluene, and a close-boiling product consisting of the isomeric xylenes, together with motor benzole, solvent naphtha, and heavy naphtha. Apart from motor benzole they find extensive use in the dye-stuffs, rubber, explosives, dry-cleaning, and paint and varnish industries, &c., both in their natural form and as a basis for the synthesis of other compounds. For further information upon the production of benzole and allied products the reader is referred to text-books on the subject, such as *Motor Benzole* by Hoffert and Claxton, and *The Principles of Motor Fuel Preparation and Application*, vol. i, by Nash and Howes. The residue in the still after removal of the light spirit from the washed crude naphtha is run off into shallow cooling pans where the naphthalene is caused to crystallize out by simple atmospheric cooling. The crystals are freed from adhering fluid oil by centrifuging or hydraulic pressing, and then subjected to purification by a method to be described later. It should be understood that we are dealing with the technique of tar distillation in a general manner, i.e. as applied to the treatment of a mixed type of tar.



The light oils, or the second fraction obtained during the primary distillation of tar, contain more phenols and naphthalene than the crude naphtha. They are washed in the same manner for the recovery of phenols and tar bases, after which the oil is cooled and the naphthalene which crystallizes out treated as before. The oil is then fractionated to recover heavy naphtha, which is purified along with the spirit from the crude naphtha, and an oil suitable for the manufacture of disinfectant fluids.

The middle oil is treated for the recovery of phenols, naphthalene, and benzole wash oils. The creosote fraction itself is not given any further treatment, but finds a ready market in its original form. Anthracene oil, on cooling, deposits crystals of crude anthracene which can be separated by means of a centrifuge or hydraulic presses and submitted to purification. This usually entails some form of solvent treatment, e.g. recrystallization from pyridine, and carbazole and phenanthrene can, if required, be obtained as by-products. Sublimation is sometimes the final step in the purification process. The oil drained from the crystals of crude anthracene is often known as green oil, because of its distinctive colour.

The pitch—that is, the residue remaining in the still at the conclusion of a complete tar distillation—is usually run into a preliminary cooler, after which it is allowed to flow into the appropriate cooling bay, of which there are usually several, fed from a single gutter or trough conveying the molten pitch from the plant. After it has been given time to solidify throughout, the pitch can be excavated in some convenient manner and dispatched to its destination. In cases where there are not several smaller bays available, the practice may be adopted of partitioning a large one, so that it can be filled in sections, thus avoiding the delay caused by filling the whole bay slowly and having to wait for the last batch to solidify before excavation can be started. The size of the bays will be governed mainly by the output of the plant and the ground space available. A pitch bay generally takes the form of a rectangular flat-bottomed pit several feet in depth with sides sloping inwards, the whole being concrete or brick lined and lime-washed to facilitate removal of the pitch after setting. Pitch is prepared on the basis of a predetermined degree of hardness, the so-called medium soft grade being most in demand, and this has a softening-point as determined by the Kraemer and Sarnow test of 65–75° C. Its uses will be discussed later with those of the remaining products.

The phenols are recovered from the bulked alkaline extracts obtained from the washing of the crude naphtha, light oils, and middle oils with NaOH solution as previously mentioned. This aqueous extract generally contains a small amount of entrained or dissolved neutral oil, naphthalene, and pyridine bases and, as the finished products are usually required to give a clear solution when mixed with NaOH solution in given proportions, these impurities are removed at this stage by solvent treatment or steam distillation—usually the latter. The purified extract is then decomposed by the action of CO_2, either in a series of tanks by simple bubbling, or by a countercurrent process in a packed tower. The gas is obtained either from a lime kiln or as a waste gas from ammonium sulphate manufacture. On settling the treated liquor, the crude phenols rise to the surface and are separated, the lower aqueous solution of sodium carbonate being recausticized with lime and returned to the oil-washing process. The crude phenols are treated with sulphuric acid of 70–80% strength to lower their water content, and at the same time neutralize any alkali present. They are then submitted to a series of fractional distillations, usually under vacuum, by which means pure phenol, a well-defined mixture of cresols, and a fraction consisting mainly of xylenols are obtained. The cresol fraction is prepared in accordance with different specifications mainly demanding certain proportions of the three isomers, ortho-, meta-, and para-cresol. In addition, pure *o*-cresol can be obtained by efficient fractionation and recrystallization, but a chemical separation is required to isolate the meta- from the para-isomer. If required, also, certain members of the xylenol group can be concentrated in close fractions.

Tar bases, or pyridine and its homologues, are found in loose combination with the sulphuric acid used for washing the crude naphtha and the light oils. For their recovery it is necessary to neutralize the sulphuric acid by some means, and on a works operating an ammonia-recovery plant this is usually carried out with gaseous ammonia. This operation is conducted in a closed vessel so that the vapours evolved owing to the heat of reaction between the ammonia and the sulphuric acid can be conducted away and condensed to avoid loss of pyridine. The solution of ammonium sulphate remaining after separation of the released bases can also be steamed to recover any of the latter remaining dissolved in the liquor, before it is sent forward to the ammonium sulphate plant. The crude bases are then steam distilled to a given point and the pyridine, &c., recovered from solution in the aqueous distillate, by treatment of the latter with strong caustic soda solution. The separated bases are dried by caustic-soda treatment and fractionated to give either pure pyridine or a mixed fraction according to specification, the general demand being for a material giving 90% distillate up to 140° C. If required, higher boiling fractions can be obtained from the still residues. In place of the ammonia, lime or soda ash may be used for neutralizing the original acid extract, the remainder of the process being similar to the above. Before neutralization, also, the acid extract should be freed from oily or resinous matter likely to impair the quality of the product.

The crude naphthalene obtained from the crude naphtha, light oil, and middle oil is treated with 3–4% by weight of strong sulphuric acid, and with caustic soda solution, to remove the impurities, after which it is fractionally distilled to give a high-grade product which is run into cooling pans and allowed to solidify. This material may be crushed and pressed into balls or tablets, or otherwise prepared for dispatch, or it may be sublimed from steam-heated pans to give a fine-flaked product. The uses of naphthalene are varied, and among the better known are those in connexion with dye-stuffs, synthetic resins, synthetic tannins, drugs, explosives, and patent fuels, and its use as an insecticide, fumigant, and general insect repellant. Recent developments have been the increased use of naphthalene for conversion into its hydrogenation products deca- and tetrahydronaphthalene, otherwise known as 'decalin' and 'tetralin' respectively, which find employment as solvents or turpentine substitutes, and the chlorination of naphthalene to yield synthetic waxes capable of wide industrial application, and said to possess excellent flameproofing and waterproofing properties. Flake naphthalene has been used as artificial snow in the cinematograph industry. For more detailed information regarding naphthalene such as its properties, constitution, &c., reference should be made to Thorpe's *Dictionary of Applied Chemistry*, suppt. vol. ii.

The phenols of high-temperature tar find extensive application nowadays in the synthetic resin industry, and thereby make contact with industries far too numerous to mention. Their disinfectant and antiseptic properties are well known, the higher homologues being more efficient in this respect, whilst the chlor-derivatives are even more effective. The cresols find one outlet in the manufacture of 'Lysol'. The phenols constitute the active agent in the emulsifying type of disinfectant previously mentioned, and consisting of a mixture of tar oil and specially prepared soap. The oil chosen for this purpose usually contains sufficient phenols in its original form, and as this type of disinfectant emulsifies when mixed with water, it generally exhibits a greater germicidal efficiency than would be expected from its composition alone, due, no doubt, to the increased area of contact resulting from dispersion into fine particles. Hydrogenation is now carried out upon phenol and the cresols with the formation of cyclohexanol and methylcyclohexanol, which substances find considerable use for general solvent purposes, particularly as plasticizers in varnishes and lacquers. Aromatic hydrocarbons can also be produced by the hydrogenation process when applied to phenols, but as far as is known no commercial developments in this direction have taken place. Triphenylphosphate and tricresyl-phosphate are other derivatives which function successfully as plasticizers, e.g. in the preparation of photographic film. Familiar uses of the phenols are, in the production of medicinals such as salicylic acid, methyl salicylate, sodium salicylate, and aspirin, in the dyestuffs industry, in the refining of lubricating oils, and in the production of photographic chemicals and synthetic tanning materials. In addition they are found in many toilet preparations, and serve as a raw material in the manufacture of synthetic perfumes, whilst in a national emergency they are in great demand for the production of explosives. The quality of the commercial phenols generally conforms to one of the following British Standard Specifications (B.S.S.): nos. 515, 516, 517, 521, 522, 523, or 524 of 1933, or to a given pharmaceutical standard. The determination of the Rideal-Walker coefficient of a fluid disinfectant, i.e. its germicidal power compared with that of pure phenol, is governed by B.S.S. no. 541–1934. It should be mentioned that, considering the phenols normally recovered from a tar in their entirety, the phenol content decreases and almost disappears, whilst the amount of cresols and higher homologues present increases as one passes in turn from horizontal-retort tar to vertical-retort tar and finally to low-temperature tar. In collaboration with the British Cotton Industries Research Association, the Chemical Research Laboratory has developed a phenolic wetting agent under the name 'Shirlacrol' which has as its basis a specially selected fraction of tar acids from vertical-retort or low-temperature tar. Phenol and its homologues have been reviewed at some length under that heading and under the heading of carbolic acid in the supplement of Thorpe's *Dictionary*.

The term creosote may be applied to a number of grades of tar oil, but, in general, it denotes the fraction shown in the chart, mixed, perhaps, as circumstances require, with a quantity of anthracene oil. Its main use is in the preservation of timber, and for this purpose it must conform to a number of specifications originating in various countries and compiled in many cases by railway authorities. In Great Britain creosote to B.S.S. no. 144–1936 is usually employed, and it is worthy of note that special provision has been made therein for 'Scottish' creosote, thus recognizing the different tar-producing qualities of Scottish coals. At one time the U.S.A. absorbed about 70% of the British production, but since 1929 its requirements have been increasingly met by home production, with the result that exports of creosote to that country during 1933 were only one-sixth that of 1929. Fortunately this has been offset to a considerable extent by increased demands from European countries and the encouragement of a home market for creosote for fuel purposes and for hydrogenation. In regard to the latter phase mention must be made of the hydrogenation plant erected by Imperial Chemical Industries at Billingham, which commenced operations with creosote as the raw material, from which substance it is proposed to produce one-third of the total motor-spirit output of the plant, which is of the order of 45 million gallons per annum. The figure of 90 million gallons for the production of creosote in the United Kingdom during 1934, compared with 72 million gallons in 1933, seems to reflect the position, even if allowance is made for the possible inclusion of low-temperature creosote in these returns. Attempts have been made to develop the use of creosote in spark-ignition engines, but after exhaustive trials by several transport companies they must at present be considered unfruitful, although valuable experience has been gained and further research may ultimately reverse the position. The use of creosote alone as a fuel for compression-ignition engines has not developed to the extent expected, mainly on account of its high spontaneous ignition temperature, but the encouragement of a tariff on imported oils will no doubt stimulate research to overcome this difficulty, either by some treatment of the oil such as the addition of a cheap primer, or by changes in engine design. Creosote can, however, be used satisfactorily as a furnace fuel, and finds considerable application in this respect, B.S.S. no. 503–1933 covering such material. Further uses of creosote are as wash oil for the recovery of benzole, &c., from coal gas, in certain ore-flotation processes, and as a fluxing medium in the production of cut-back bitumens.

The main use of pitch is as a binder in the manufacture of coal briquettes. Its use in this connexion will doubtless continue, although attempts are being made to dispense with the binder and utilize the plastic properties of the coal substance. In the manufacture of briquettes the importance of the size of the coal particles has been recognized, whilst recent work upon different pitches [4, 1933; 5, 1933; 23, 1935] has shown that the softening-point alone is not a sufficient criterion of the briquetting properties of a pitch. Briquetting pitches have been resolved into fractions by solvent treatment in a manner similar to that quoted for tar and their compositions compared on the basis of the strength of the corresponding briquettes. By this means it has been found possible to specify an optimum average composition for a good briquetting pitch. Pitch has its uses also in the building and electrical trades, either as a waterproofing or insulating medium, whilst it answers a similar purpose when adopted in some form as a protective coating for underground pipes. Pitch coking, a number of processes for which are available, produces a coke well suited to the requirements of the electrical industry. Black paints, varnishes, and enamels often contain pitch as an ingredient.

Tar bases, regarding whose use no mention has yet been made, find employment mainly as solvents, as a denaturant for alcohol, and as a raw material in the production of rubber accelerators of the piperidine class.

For the sampling of coal tar and its products the reader is referred to B.S.S. no. 616–1935, and for testing and analysis to *Standard Methods for Testing Tar and its Products* published by the Standardization of Tar Products Tests Committee, 166 Piccadilly, London, W. 1.

For an account of the historical development of the coal-tar industry, the publications of Accum [2, 1818] and Lunge [16, 1887] should be consulted (see also Heydenreich [11, 1931] and Malatesta [17, 1920]).

*World production of crude coal tar. Million tons**		*Consumption of road tar by various countries. Tons**				
			France	*Germany*	*U.S.A.*	*Great Britain*
1927	7·5	1924	97,000	3,000	..	..
		1925	135,000	12,000	..	..
1928	8·2	1926	157,000	60,000	..	..
		1927	182,000	85,000	..	700,000
1929	8·8	1928	239,000	97,000	..	..
		1929	367,000	120,000	500,000	750,000
1930	8·0	1930	450,000	151,000	..	..
		1931	469,000	117,000	..	..
1931	6·8	1932	520,000	125,000	..	..
		1933	513,000	150,000	600,000	875,000

World Production of Crude Tar

Country	*Amount in 1,000 tons**				
	1927	*1929*	*1931*	*1933*	*1934*
United States	2,490	3,020	2,050	1,550	2,200
Great Britain	1,810	1,980	1,660	1,600	1,750
Germany	1,500	1,750	1,100	1,150	1,250
France (incl. Saar)	590	690	680	642	672
Soviet Russia	75	110	150–200	..	..
Belgium	190	200	175	150	..
Canada	110	130	110	..	..
Czechoslovakia	110	130	110	110	..
Netherlands	70	90	100	130	..
Australia	100	110	100	..	128
Japan	80	100	..	..	..
Poland	80	100	80	130	96†
Italy	45	50	50	90	91
Spain	40	45	40	80	..
Austria	30	40	30	..	..
Switzerland	30	40	30	28	..

*Consumption of Road Tar by Various Countries in 1933**

Belgium	10,000 tons	Switzerland	13,000 tons
Holland	11,000 „	Spain	8,000 „
Italy	14,000 „	Czechoslovakia	8,000 „

* Figures given represent metric tons.

† 1935.

REFERENCES

1. *Account of the Qualities and Uses of Coal Tar and Coa Varnish with Certificates from Ship Masters and Others* (London, 1785).
2. Accum, F. *A Practical Treatise on Gas Light*, 4th ed. (1818).
3. Adam, W. G., and Sach, J. S. *J.S.C.I.* **48**, 337T (1929).
4. Broche, H., and Nedelmann, H. *Glückauf*, **69**, 12, 257 (1933); *Gas J.* **202**, 109 (1933).
5. Demann, W. *Brenn.-Chem.* **14**, 121 (1933); *Brit. Chem. Abs.* 417B (1933).
6. Donath, E., and Asriel, M. *Chem. Zent.* **74**, (1) 1099 (1903).
7. Edwards, J. Prepared Tars and their Application to Road Construction. *Gas World*, 102, 167, (1935).
8. Fieldner, A. C., and Davis, J. D. *Gas-, Coke-, and By-product-making Properties of American Coals and their Determination.* U.S. Bureau of Mines, Monograph 5.
9. Gas, Light, and Coke Co., Adam, W. G., Murdoch, D. G., and Potter, F. M. B.P. 408,275 (1932).
10. Gas, Light, and Coke Co., Adam, W. G., and Potter, F. M. B.P. 303,038 (1927).
11. Heydenreich, F. A. *Die deutsche Steinkohlenteerindustrie und ihre wirtschaftlichen Zusammenhänge* (1931).
12. Highways and Bridges, 19 June 1935.
13. Hoffert, W. H., and Claxton, G. Modern Methods of Benzol Refining. The Use of Inhibitors for preventing Gum Formation. *J.S.C.I.* **52**, 25T (1933), and *Proc. World Petr. Cong.* **2**, 69–76 (1933).
14. Hollings, H. *J.S.C.I.* **45**, 406T (1926).
15. Hunter, R. W. *Gas World*, **98**, 520 (1933).
16. Lunge, G. *Coal Tar and Ammonia*, 2nd ed. (1887).
17. Malatesta, G. *Coal Tars and their Derivatives* (1920).
18. Marcusson, J. *Chem.-Ztg.* **54**, 795 (1930).
19. ——— *Angew. Chem.* **32** (1), 385 (1919).
20. Morgan, G. T., Pratt, D. D., and Ross, J. A. Chemical Study of Low Temperature Tar. *J.S.C.I.* **48**, 29T (1929).
21. Nellensteyn, F. J., and Kuipers, J. P. Die Micronenzahl. *Teer u. Bitumen*, **31**, 309 (1933).
22. *Proc. Amer. Soc. Testing Mat.* **11**, 665 (1911).
23. Reerink, W., and Goecke, E. *Glückauf*, **71**, 77–85 and 105–14 (1935); *Gas J.* **209**, 510 (1935).
24. U.S. Bureau of Mines, Report of Investigations, R.I. 3197 (1932).
25. Warnes, A. R. *Coal Tar Distillation*, 3rd ed. (1923).
26. Weise, E. Modern Methods of Tar Distillation. *Petroleum*, **26**, 499–504, 577–82 (1930).
27. Weiss, J. M. The Distillation of Coal Tar. *J.S.C.I.* **51**, 219–23 and 246–50 (1932).
28. Weiss, J. *Ind. Eng. Chem.* **6**, 279 (1914).
29. Wilton, T. O. B.P. 424,645 (1933).

APPENDIX

See Vol. II, p. 1156

('Determination of Density and Refractive Index of Hydrocarbons and Petroleum Products' by A. L, **WARD, S. S. KURTZ, Jr.,** and **W. H. FULWEILER.**)

Reduction of Observed Degrees API. to Degrees API. at 60° F.

Observed temperature in °F.	*Observed degrees API.*									
	0	1	2	3	4	5	6	7	8	9
	Corresponding degrees API. at 60° F.									
0	2·5	3·5	4·6	5·7	6·7	7·8	8·8	9·9	11·0	12·0
1	2·4	3·5	4·6	5·6	6·7	7·7	8·8	9·9	10·9	12·0
2	2·4	3·5	4·5	5·6	6·6	7·7	8·8	9·8	10·9	11·9
3	2·4	3·4	4·5	5·5	6·6	7·6	8·7	9·8	10·8	11·9
4	2·3	3·4	4·4	5·5	6·5	7·6	8·7	9·7	10·8	11·8
5	2·3	3·3	4·4	5·4	6·5	7·6	8·6	9·7	10·7	11·8
6	2·2	3·3	4·3	5·4	6·5	7·5	8·6	9·6	10·7	11·7
7	2·2	3·2	4·3	5·4	6·4	7·5	8·5	9·6	10·6	11·7
8	2·2	3·2	4·3	5·3	6·4	7·4	8·5	9·5	10·6	11·6
9	2·1	3·2	4·2	5·3	6·3	7·4	8·4	9·5	10·5	11·6
10	2·1	3·1	4·2	5·2	6·3	7·3	8·4	9·4	10·5	11·5
11	2·0	3·1	4·1	5·2	6·2	7·3	8·3	9·4	10·4	11·5
12	2·0	3·0	4·1	5·1	6·2	7·2	8·3	9·3	10·4	11·4
13	1·9	3·0	4·0	5·1	6·1	7·2	8·2	9·3	10·3	11·4
14	1·9	2·9	4·0	5·0	6·1	7·1	8·2	9·2	10·3	11·3
15	1·9	2·9	3·9	5·0	6·0	7·1	8·1	9·2	10·2	11·3
16	1·8	2·9	3·9	4·9	6·0	7·0	8·1	9·1	10·2	11·2
17	1·8	2·8	3·9	4·9	5·9	7·0	8·0	9·1	10·1	11·2
18	1·7	2·8	3·8	4·9	5·9	6·9	8·0	9·0	10·1	11·1
19	1·7	2·7	3·8	4·8	5·9	6·9	7·9	9·0	10·0	11·1
20	1·7	2·7	3·7	4·8	5·8	6·9	7·9	8·9	10·0	11·0
21	1·6	2·7	3·7	4·7	5·8	6·8	7·9	8·9	9·9	11·0
22	1·6	2·6	3·6	4·7	5·7	6·8	7·8	8·8	9·9	10·9
23	1·5	2·6	3·6	4·6	5·7	6·7	7·8	8·8	9·8	10·9
24	1·5	2·5	3·6	4·6	5·6	6·7	7·7	8·7	9·8	10·8
25	1·5	2·5	3·5	4·6	5·6	6·6	7·7	8·7	9·7	10·8
26	1·4	2·4	3·5	4·5	5·5	6·6	7·6	8·6	9·7	10·7
27	1·4	2·4	3·4	4·5	5·5	6·5	7·6	8·6	9·6	10·7
28	1·3	2·3	3·4	4·4	5·4	6·5	7·5	8·5	9·6	10·6
29	1·3	2·3	3·3	4·4	5·4	6·4	7·5	8·5	9·5	10·6
30	1·2	2·3	3·3	4·3	5·3	6·4	7·4	8·4	9·5	10·5
31	1·2	2·2	3·2	4·3	5·3	6·3	7·4	8·4	9·4	10·4
32	1·1	2·2	3·2	4·2	5·3	6·3	7·3	8·3	9·4	10·4
33	1·1	2·1	3·2	4·2	5·2	6·2	7·3	8·3	9·3	10·3
34	1·1	2·1	3·1	4·1	5·2	6·2	7·2	8·2	9·3	10·3
35	1·0	2·0	3·1	4·1	5·1	6·1	7·2	8·2	9·2	10·2
36	1·0	2·0	3·0	4·0	5·1	6·1	7·1	8·1	9·2	10·2
37	0·9	2·0	3·0	4·0	5·0	6·0	7·1	8·1	9·1	10·1
38	0·9	1·9	2·9	4·0	5·0	6·0	7·0	8·0	9·1	10·1
39	0·9	1·9	2·9	3·9	4·9	6·0	7·0	8·0	9·0	10·0
40	0·8	1·8	2·9	3·9	4·9	5·9	6·9	7·9	9·0	10·0
41	0·8	1·8	2·8	3·8	4·8	5·9	6·9	7·9	8·9	9·9
42	0·7	1·7	2·8	3·8	4·8	5·8	6·8	7·8	8·9	9·9
43	0·7	1·7	2·7	3·7	4·7	5·8	6·8	7·8	8·8	9·8
44	0·7	1·7	2·7	3·7	4·7	5·7	6·7	7·7	8·8	9·8
100	..	..	0·3	1·3	2·3	3·2	4·2	5·2	6·1	7·1
101	..	..	0·3	1·2	2·2	3·2	4·2	5·1	6·1	7·1
102	..	..	0·2	1·2	2·2	3·1	4·1	5·1	6·0	7·0
103	..	..	0·2	1·2	2·1	3·1	4·1	5·0	6·0	7·0
104	..	..	0·1	1·1	2·1	3·1	4·0	5·0	5·9	6·9
105	..	..	0·1	1·1	2·0	3·0	4·0	4·9	5·9	6·9
106	..	..	0·1	1·0	2·0	3·0	3·9	4·9	5·9	6·8
107	..	..	0·0	1·0	2·0	2·9	3·9	4·8	5·8	6·8
108	..	..	..	1·0	1·9	2·9	3·8	4·8	5·8	6·7
109	..	..	..	0·9	1·9	2·8	3·8	4·8	5·7	6·7
110	..	..	..	0·9	1·8	2·8	3·8	4·7	5·7	6·6
111	..	..	..	0·8	1·8	2·7	3·7	4·7	5·6	6·6
112	..	..	..	0·8	1·7	2·7	3·7	4·6	5·6	6·5
113	..	..	..	0·7	1·7	2·7	3·6	4·6	5·5	6·5
114	..	..	..	0·7	1·7	2·6	3·6	4·5	5·5	6·4
115	..	..	..	0·7	1·6	2·6	3·5	4·5	5·4	6·4
116	..	..	..	0·6	1·6	2·5	3·5	4·4	5·4	6·4
117	..	..	..	0·6	1·5	2·5	3·4	4·4	5·4	6·3
118	..	..	..	0·5	1·5	2·4	3·4	4·3	5·3	6·3
119	..	..	..	0·5	1·4	2·4	3·4	4·3	5·3	6·2
120	..	..	..	0·4	1·4	2·4	3·3	4·3	5·2	6·2
121	..	..	..	0·4	1·4	2·3	3·3	4·2	5·2	6·1
122	..	..	..	0·4	1·3	2·3	3·2	4·2	5·1	6·1
123	..	..	.	0·3	1·3	2·2	3·2	4·1	5·1	6·0
124	..	..	..	0·3	1·2	2·2	3·1	4·1	5·0	6·0
125	..	..	..	0·2	1·2	2·1	3·1	4·0	5·0	5·9
126	..	..	..	0·2	1·1	2·1	3·0	4·0	4·9	5·9
127	..	..	..	0·2	1·1	2·1	3·0	4·0	4·9	5·9
128	..	..	..	0·1	1·1	2·0	3·0	3·9	4·9	5·8
129	..	.	..	0·1	1·0	2·0	2·9	3·9	4·8	5·8
130	..	..	..	0·0	1·0	1·9	2·9	3·8	4·8	5·7
131	..	..	..	..	0·9	1·9	2·8	3·8	4·7	5·7
132	..	..	..	..	0·9	1·8	2·8	3·7	4·7	5·6
133	..	..	..	..	0·9	1·8	2·8	3·7	4·6	5·6
134	..	..	..	..	0·8	1·8	2·7	3·7	4·6	5·5
135	..	..	..	..	0·8	1·7	2·7	3·6	4·6	5·5
136	..	..	..	..	0·7	1·7	2·6	3·6	4·5	5·5
137	..	..	..	..	0·7	1·6	2·6	3·5	4·5	5·4
138	..	..	..	..	0·7	1·6	2·5	3·5	4·4	5·4
139	..	..	..	..	0·6	1·6	2·5	3·5	4·4	5·3
140	..	..	..	..	0·6	1·5	2·5	3·4	4·4	5·3
141	..	..	..	..	0·5	1·5	2·4	3·4	4·3	5·2
142	..	..	..	..	0·5	1·4	2·4	3·3	4·3	5·2
143	..	..	..	..	0·5	1·4	2·3	3·3	4·2	5·2
144	..	..	..	..	0·4	1·3	2·3	3·2	4·2	5·1

45	0·6	1·6	2·6	3·6	4·7	5·7	6·7	7·7	8·7	9·7
46	0·6	1·6	2·6	3·6	4·6	5·6	6·6	7·7	8·7	9·7
47	0·5	1·5	2·5	3·6	4·6	5·6	6·6	7·6	8·6	9·6
48	0·5	1·5	2·5	3·5	4·5	5·5	6·5	7·6	8·6	9·6
49	0·5	1·5	2·5	3·5	4·5	5·5	6·5	7·5	8·5	9·5
50	0·4	1·4	2·4	3·4	4·4	5·5	6·5	7·5	8·5	9·5
51	0·4	1·4	2·4	3·4	4·4	5·4	6·4	7·4	8·4	9·4
52	0·3	1·3	2·3	3·4	4·4	5·4	6·4	7·4	8·4	9·4
53	0·3	1·3	2·3	3·3	4·3	5·3	6·3	7·3	8·3	9·3
54	0·2	1·3	2·3	3·3	4·3	5·3	6·3	7·3	8·3	9·3
55	0·2	1·2	2·2	3·2	4·2	5·2	6·2	7·2	8·2	9·2
56	0·2	1·2	2·2	3·2	4·2	5·2	6·2	7·2	8·2	9·2
57	0·1	1·1	2·1	3·1	4·1	5·1	6·1	7·1	8·1	9·1
58	0·1	1·1	2·1	3·1	4·1	5·1	6·1	7·1	8·1	9·1
59	0·0	1·0	2·0	3·0	4·0	5·0	6·0	7·0	8·0	9·0
60	0·0	1·0	2·0	3·0	4·0	5·0	6·0	7·0	8·0	9·0
61	..	1·0	2·0	3·0	4·0	5·0	6·0	7·0	8·0	9·0
62	..	0·9	1·9	2·9	3·9	4·9	5·9	6·9	7·9	8·9
63	..	0·9	1·9	2·9	3·9	4·9	5·9	6·9	7·9	8·9
64	..	0·8	1·8	2·8	3·8	4·8	5·8	6·8	7·8	8·8
65	..	0·8	1·8	2·8	3·8	4·8	5·8	6·8	7·8	8·8
66	..	0·7	1·7	2·7	3·7	4·7	5·7	6·7	7·7	8·7
67	..	0·7	1·7	2·7	3·7	4·7	5·7	6·7	7·7	8·7
68	..	0·7	1·7	2·7	3·6	4·6	5·6	6·6	7·6	8·6
69	..	0·6	1·6	2·6	3·6	4·6	5·6	6·6	7·6	8·6
70	..	0·6	1·6	2·6	3·6	4·6	5·5	6·5	7·5	8·5
71	..	0·5	1·5	2·5	3·5	4·5	5·5	6·5	7·5	8·5
72	..	0·5	1·5	2·5	3·5	4·5	5·4	6·4	7·4	8·4
73	..	0·5	1·4	2·4	3·4	4·4	5·4	6·4	7·4	8·4
74	..	0·4	1·4	2·4	3·4	4·4	5·4	6·3	7·3	8·3
75	..	0·4	1·4	2·4	3·3	4·3	5·3	6·3	7·3	8·3
76	..	0·3	1·3	2·3	3·3	4·3	5·3	6·2	7·2	8·2
77	..	0·3	1·3	2·3	3·2	4·2	5·2	6·2	7·2	8·2
78	..	0·3	1·2	2·2	3·2	4·2	5·2	6·2	7·1	8·1
79	..	0·2	1·2	2·2	3·2	4·1	5·1	6·1	7·1	8·1
80	..	0·2	1·1	2·1	3·1	4·1	5·1	6·1	7·1	8·0
81	..	0·1	1·1	2·1	3·1	4·1	5·1	6·0	7·0	8·0
82	..	0·1	1·1	2·1	3·0	4·0	5·0	6·0	7·0	8·0
83	..	0·0	1·0	2·0	3·0	4·0	5·0	5·9	6·9	7·9
84	..	..	1·0	2·0	2·9	3·9	4·9	5·9	6·9	7·9
85	..	..	0·9	1·9	2·9	3·9	4·9	5·9	6·8	7·8
86	..	..	0·9	1·9	2·9	3·8	4·8	5·8	6·8	7·8
87	..	..	0·9	1·8	2·8	3·8	4·8	5·8	6·7	7·7
88	..	..	0·8	1·8	2·8	3·8	4·7	5·7	6·7	7·7
89	..	..	0·8	1·8	2·7	3·7	4·7	5·7	6·6	7·6
90	..	..	0·7	1·7	2·7	3·7	4·6	5·6	6·6	7·6
91	..	..	0·7	1·7	2·6	3·6	4·6	5·6	6·5	7·5
92	..	..	0·6	1·6	2·6	3·6	4·6	5·5	6·5	7·5
93	..	..	0·6	1·6	2·6	3·5	4·5	5·5	6·4	7·4
94	..	..	0·6	1·5	2·5	3·5	4·5	5·4	6·4	7·4
95	..	..	0·5	1·5	2·5	3·4	4·4	5·4	6·4	7·3
96	..	..	0·5	1·4	2·4	3·4	4·4	5·3	6·3	7·3
97	..	..	0·4	1·4	2·4	3·4	4·3	5·3	6·3	7·2
98	..	..	0·4	1·4	2·3	3·3	4·3	5·2	6·2	7·2
99	..	..	0·3	1·3	2·3	3·3	4·2	5·2	6·2	7·1
145	..	..	..	..	0·4	1·3	2·3	3·2	4·1	5·1
146	..	..	..	..	0·3	1·3	2·2	3·2	4·1	5·0
147	..	..	..	..	0·3	1·2	2·2	3·1	4·1	5·0
148	..	..	..	..	0·2	1·2	2·1	3·1	4·0	4·9
149	..	..	..	..	0·2	1·1	2·1	3·0	4·0	4·9
150	..	..	..	..	0·2	1·1	2·1	3·0	3·9	4·9
151	..	..	..	..	0·1	1·1	2·0	3·0	3·9	4·8
152	..	..	..	..	0·1	1·0	2·0	2·9	3·8	4·8
153	..	..	..	..	0·0	1·0	1·9	2·9	3·8	4·7
154	..	..	..	..	..	0·9	1·9	2·8	3·7	4·7
155	..	..	..	..	..	0·9	1·8	2·8	3·7	4·6
156	..	..	..	..	..	0·9	1·8	2·7	3·7	4·6
157	..	..	..	..	..	0·8	1·8	2·7	3·6	4·5
158	..	..	..	..	..	0·8	1·7	2·7	3·6	4·5
159	..	..	..	..	..	0·7	1·7	2·6	3·5	4·5
160	..	..	..	..	..	0·7	1·6	2·6	3·5	4·4
161	..	..	..	..	..	0·7	1·6	2·5	3·5	4·4
162	..	..	..	..	..	0·6	1·6	2·5	3·4	4·3
163	..	..	..	..	..	0·6	1·5	2·5	3·4	4·3
164	..	..	..	..	..	0·5	1·5	2·4	3·3	4·3
165	..	..	..	..	..	0·5	1·4	2·4	3·3	4·2
166	..	..	..	..	..	0·5	1·4	2·3	3·3	4·2
167	..	..	..	..	..	0·4	1·4	2·3	3·2	4·1
168	..	..	..	..	..	0·4	1·3	2·3	3·2	4·1
169	..	..	..	..	..	0·3	1·3	2·2	3·1	4·1
170	..	..	..	..	..	0·3	1·2	2·2	3·1	4·0
171	..	..	..	..	..	0·3	1·2	2·1	3·1	4·0
172	..	..	..	..	..	0·2	1·2	2·1	3·0	3·9
173	..	..	..	..	..	0·2	1·1	2·0	3·0	3·9
174	..	..	..	..	..	0·1	1·1	2·0	2·9	3·9
175	..	..	..	..	..	0·1	1·0	2·0	2·9	3·8
176	..	..	..	..	..	0·1	1·0	1·9	2·9	3·8
177	..	..	..	..	..	0·0	1·0	1·9	2·8	3·7
178	..	..	..	..	..	..	0·9	1·9	2·8	3·7
179	..	..	..	..	..	..	0·9	1·8	2·7	3·7
180	..	..	..	..	..	..	0·8	1·8	2·7	3·6
181	..	..	..	..	..	..	0·8	1·7	2·7	3·6
182	..	..	..	..	..	..	0·8	1·7	2·6	3·5
183	..	..	..	..	..	..	0·7	1·7	2·6	3·5
184	..	..	..	..	..	..	0·7	1·6	2·5	3·4
185	..	..	..	..	..	..	0·6	1·6	2·5	3·4
186	..	..	..	..	..	..	0·6	1·5	2·4	3·4
187	..	..	..	..	..	..	0·6	1·5	2·4	3·3
188	..	..	..	..	..	..	0·5	1·4	2·4	3·3
189	..	..	..	..	..	..	0·5	1·4	2·3	3·2
190	..	..	..	..	..	..	0·4	1·4	2·3	3·2
191	..	..	..	..	..	..	0·4	1·3	2·2	3·2
192	..	..	..	..	..	..	0·4	1·3	2·2	3·1
193	..	..	..	..	..	..	0·3	1·2	2·2	3·1
194	..	..	..	..	..	..	0·3	1·2	2·1	3·0
195	..	..	..	..	..	..	0·2	1·2	2·1	3·0

INDEXES

INDEX OF CONTRIBUTORS

INDEX OF NAMES

INDEX OF SUBJECTS

PRINTED IN
GREAT BRITAIN
AT THE
UNIVERSITY PRESS
OXFORD
BY
JOHN JOHNSON
PRINTER
TO THE
UNIVERSITY

For Reference

NOT TO BE TAKEN FROM THIS ROOM.