LUBRICATING AND ALLIED OILS

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by

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Foreword by the late
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OF HYTHE
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FOREWORD

By the Late Viscount Wakefield of Hythe, G.C.V.O., LL.D., etc.

The art of Lubrication is comparatively old, but it is only since the discovery of mineral oil that it has come to be known as a science. Having in view its importance to industry, little has been written on the subject, which is one of some complexity, demanding the threefold co-operation of Chemist, Engineer, and Physicist.

Though the theory of lubrication leaves much to be understood, good progress is being made by research into the relationship between chemical constitution and friction. The Engineer also is contributing his quota in determining the best way of applying the lubricant.

The actual user of lubricating oils has been handicapped in the past through want of expert guidance and has had to draw on his own experience or on that of his friends or rely upon the advice of the Oil Manufacturer, which, though in the main good, leaves much that is lacking. It is to meet this want that Mr. Elliott A. Evans has in this treatise laid bare the fundamental considerations in the selection of a lubricant.

Such a book, written by one whose experience in all branches of the subject is beyond question, should commend itself to a wide range of readers.

PREFACE TO THIRD EDITION

THE style of this book has been maintained and its scope preserved but this edition has been completely rewritten. Much has been omitted, and new chapters have been introduced. Fatty oils have been described in a manner which should give chemists a better appreciation of their constitution and behaviour. The ugly question of engine deposits has found a place and been discussed in such a way as to make it intelligible. Since the last edition was published chemical addition agents have appeared. Although the subject is so new and complex, an introductory survey is given.

Probably nothing has focused more attention upon lubrication more than the General Discussion on Lubrication organised by the Institution of Mechanical Engineers in 1937. Papers were contributed by well-known scientists from many parts of the world. In any study of the subject these papers cannot be ignored, and no book would be complete without references to them. The Institute of Petroleum has completely revised Standard Methods for Testing Petroleum Products, and has now placed the methods on a very satisfactory basis. In addition, the scientific journals continue to provide new theories and the results of research. From these publications matter has been drawn and acknowledged as far as possible. Unfortunately it is not easy to pay tribute to every source of information, but it is done so now in general but grateful terms.

ELLIOTT A. EVANS

PREFACE TO SECOND EDITION

DURING the years which have elapsed since 1921 a vast amount of literature has appeared upon the subject of lubrication and lubricants. It is no exaggeration to state that the subject has now been established on a sound scientific foundation. The Department of Scientific and Industrial Research has been instrumental in encouraging research of a fundamental character, which has been of great value in elucidating the experimental results obtained by the Air Ministry on petrol engines, the War Office on mechanical transport, and the Admiralty in several specialised fields of research. The large engineering companies have realised the material gain to be derived from investigations in this branch of science, and the oil companies have made their contribution to the store of information.

Workers in the field of lubrication have been active in many parts of the world, especially in the United States of America.

Naturally there are still many obscure problems, and much which is controversial. In this book I have endeavoured to maintain the original scope of the work, and to avoid dogmas.

PREFACE TO FIRST EDITION

After repeated requests from chemists, engineers, and others, for a useful not too technical book on lubricating oils, the author was prompted and urged by Mr. Clifford, Librarian to the Chemical Society, London, to write a book on the subject with a view to assisting chemists in compiling specifications and examining lubricating oils, also to give engineers an insight into the application and properties of such oils, and the interpretation of their specifications. The very comprehensive book, *Lubricants and Lubrication*, by Archbutt and Deeley, is too technical except for the specialist or the person who desires knowledge on a specific section of the subject. The several books on oils, such as *Chemical Technology and Analysis of Oils, Fats, and Waxes*, by Lewkowitch, and *Treatise on Petroleum*, by Redwood, cover their sphere admirably, but they do not provide that information for which the author has been repeatedly asked. Chemists require detailed information of the methods, both physical and chemical, used in the laboratory to examine the oils, and to be in a position to pass an opinion upon their relative merits; whereas the engineer must be in a position to understand the chemist's report and to put the oil to a practical test with an appreciation of the material which he has under supervision. With these facts in mind it has been the author's endeavour to include only those tests which are commonly demanded and a discussion of those branches of the subject which are of general interest, and to exclude anything which is controversial or highly technical.

The subject-matter has been drawn from the author's experience and close association with the science of lubrication both in the laboratory and the workshop, also from numerous technical journals, papers, and books. Wherever possible the name of the author and the source of reference is given in the text.

With the valuable assistance of Mr. Clark (draughtsman to Messrs. C. C. Wakefield & Co., Ltd.) and Messrs. A. Gallenkamp & Co., Ltd., explanatory drawings have been inserted. Throughout the writing of this book much encouragement has been given by numerous friends and by Messrs. C. C. Wakefield & Co., Ltd. To them profound thanks are offered.

In conclusion, the author would be grateful for the notification of any errors which the reader may observe; or for suggested methods of increasing the value of future editions.

ELLIOTT A. EVANS

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CHAPTER I

HISTORY OF PETROLEUM

It is difficult to find a solitary individual to whom oil is not of value and interest; in fact it is perhaps impossible to imagine how any article could be in more universal demand than petroleum and the many commodities of commerce which are derived from it. The demand for oil dates back to prehistoric times, but it is only within this century that the petroleum industry has expanded to its present gigantic dimensions.

The petroleum industry is often regarded as having its birth in the discovery made by James Young that petroleum could be obtained by the distillation of certain rocks, but there is evidence that petroleum was known and used two or three thousand years before Christ. Excavators in Assyria have found excellently preserved walls cemented with bitumen which have probably stood thirty-five centuries.

According to modern translations of the Bible the words slime and salt have in many cases been substituted for the word bitumen. Thus "slime had they for mortar" in the building of the Tower of Babel is perhaps the earliest reference to bitumen in the Scriptures. This interpretation places a new construction upon the fate of Lot's wife, who, on looking back on the burning cities of Sodom and Gomorrah, stumbled into a bitumen pit.

The mythical conception of the origin of petroleum is interesting, as it constitutes the earliest record of the origin of petroleum. Prometheus was chained on the Caucasus Mountains for stealing the fire of heaven. During his captivity an eagle unceasingly devoured his liver, and afterwards vomited a black liquor which the Greeks called naphtha.

In view of the development of the Iranian oilfield, the words of Herodotus might claim attention, as they are the first description of a regular petroleum industry. "At Ardericca is a well that produces three different substances; for asphalt, salt and oil are drawn up from it in the following manner: it is pumped up by means of a swipe, and instead of a bucket, half a wineskin is attached to it. Having dipped down with the swipe, a man draws it up and pours the contents into a reservoir, and being poured from this into another, it assumes three different forms. The asphalt and the salt immediately become solid, but the oil they collect; it is black and emits a strong odour."

Probably the earliest manifestation of lubrication was found on carvings on the Egyptian tomb of Ra-Em-Ka, 2600–1700 B.C. A sledge is shown being used to transport a stone monument, and a man pouring a liquid to lubricate the runners of the sledge. Fatty matter was actually found on the axle of a chariot buried in the tomb of Yuaa and Thuiu about 1400 B.C. Pliny records that the ancients, before this time, used hog fat to lubricate the wheels of their chariots.

It is to the Romans that we are indebted for the oldest record of petroleum being used as an illuminant. The oil obtained from Agrigentum, Sicily, was used in the lamps in the temple of Jupiter.

The Greek writers also refer to petroleum. Plutarch records its discovery on the banks of the Oxus River by a servant of Alexander the Great. The Chinese describe the use of petroleum two thousand years ago, and in India the use of Rangoon oil has been known for a long time.

The petroleum industry has had a long and interesting career. The history of the Baku oilfield is associated with the fire worshippers, who about the year 600 B.C. commenced to make pilgrimages to the eternal fires. The petroleum fires of the Apsheron Peninsula being well known to the people of Persia, and the district forming part of the Persian dominions, and being accessible, the assumption is that from the earliest years of the Zoroastrian period the worshippers of fire went to Baku to the petroleum flames springing naturally from the soil.

The fires were simply burning natural gas which was emitted from the earth. To us it is commonplace to see gas burning, but to the heathen it must have appeared a very wonderful and awe-inspiring sight to see a fire fed with invisible fuel, and burning from time immemorial.

Historical evidence that the petroleum was used is lacking, although it probably was, until A.D. 950, when the Arab writer, Masudi, wrote a brief description of the district. Marco Polo described the Baku oil industry as he found it in the twelfth century. He stated that there was a great fountain of oil from which a hundred shiploads might be taken at one time. The oil was used for burning, and for this purpose was sought by people from great distances. After the annexation of Baku by Russia from Persia, Peter the Great organised a systematic transportation of petroleum to the interior of Russia, but owing to the subsequent restoration of Baku to Persia, the interests of the industry fell to other hands which worked for its advancement. By the middle of the eighteenth century it was in such abundant supply that it was used even by the humblest people, and was exported to India. In 1800 about 120,000 barrels of oil were exported, the whole of the oil being obtained from springs. In 1801 the Russian Government controlled the industry, and it was not released until 1872, since when it has gradually developed, mainly under the influence of the Nobel Bros., until recent times, when other commercial interests took control. State ownership was declared after the Great Revolution.

About 1400 a concession was made for the collection of petroleum near Miano, in Italy, and about 1,600 wells were made, 50 to 60 feet deep, at Modena, and in the early part of the nineteenth century Genoa was lighted with oil from Amiano.

The first occasion on which large-scale distillation appears to have been practised was at Prague in 1810, when the oil was distilled to obtain illuminating oil. Whether the distillation of oil shale was commenced in Great Britain the author does not know, but the fact that oil could be obtained from stone tells its own story in a patent which was granted late in the seventeenth century for a method for the production of pitch, tar and oil from a kind of stone. The oil obtained was sold as Betton's British Oil to cure rheumatism.

When the white settlers landed in America they found that the Indians had dug wells to obtain oil, which they called Seneca oil, and used it for all sorts of ills. Most of the oil wells in America emitted brine, consequently, the salt was more important to the Indians than the oil in those days; in fact the oil was regarded as a nuisance. In 1826 Hilldreth suggested that the oil be used as an illuminant instead of sperm oil. Of course, the petroleum which was used must have made the atmosphere very unattractive after lighting-up time.

The birth of the modern petroleum industry dates from the period immediately preceding 1850, when the pharmacist Kier, of Pittsburg, sold petroleum for medicinal purposes. In 1846 Gesner made an illuminating oil from coal by distillation in Prince Edward Island, and introduced it under the name "kerosene." Kier immediately conceived the idea that petroleum would be converted into a better illuminant if it were distilled. He found it to be a great success. Then his knowledge of combustion suggested to him that a lamp fitted with a glass chimney would overcome most of their troubles, and it did. Kier, possessing commercial acumen, made the label on his bottle as attractive as possible, and showed on it some derricks. Bissell was struck by these derricks, and thought that it might be possible to bore for petroleum in much the same way as artesian wells are bored.

The famous patent granted to James Young in 1850 is a landmark in the modern petroleum industry. Lord Playfair drew Young's attention to a viscous substance oozing into a coal mine at Alfreton, Derbyshire, which, on examination, proved to be crude petroleum. Young commenced to distil the crude oil to obtain illuminating oil. At first the yield was about 300 gallons per day, but in two years the flow ceased.

The laurels for further development went to America, for Bissell entrusted the boring of a well at Oil Creek, Pennsylvania, to a conductor on the New York and Newhaven Railroad by the name of Drake. Drake encountered many difficulties, mainly through the sides falling in, so he thought of the idea of driving a pipe down through the ground to stop the sides from collapsing. Drake employed an old salt well digger, old Billy Smith, to assist in the work. These two characters have become historic, as they drilled what we now regard as the first petroleum well in 1859. They struck oil at a depth of 69½ feet. The daily output from the well was 840 gallons, and it continued for one year. Drake failed to grasp the importance of his success, and let pass the opportunity of gaining great wealth. He died after being in receipt of a State pension of $1,500 per annum.

Very shortly after Drake's success there was a wild rush to Oil Creek to seek oil. These early adventurers were not rewarded handsomely for their enthusiasm, because the conditions were much too primitive, and transport too hazardous. Oilfields were discovered in other parts of the world, and developed, and methods of refining crystallised into more perfect shape, and so the industry grew, until now it is one of the greatest industries in the world. In 1860 the world's production of crude oil was 500,000 barrels, and in 1937 it had increased to the stupendous figure of 2,034,030,000 barrels.

The nineteenth century was a period of mechanical achievement. The steam engine had taken the place of animal, wind and water power. It opened a new chapter in mechanical sciences, and brought to the market new and cheaper lubricants. In the pre-petroleum days the only lubricants which were available were the common fatty oils such as tallow, rape, castor and fish oils. To indicate how the people were thinking in those days, it is interesting to note that in 1831 Booth patented a lubricant consisting of tallow, palm oil, sodium carbonate and water. By the middle of the century there was a search for larger supplies of cottonseed, whale and rosin oils. Through the increasing demand, secret and patented lubricants quickly followed, and the field was opened to mineral oils. The advent of the motor-car, and of course the internal combustion engine, gave the petroleum industry a marvellous opportunity, an opportunity which it seized, and did it justice. Without the petroleum industry, it is probably true to say the internal combustion engine could not have developed to its present state of efficiency.

To satisfy a question which is often asked, it is useful to have reproduced a list of the consumption of lubricants in various countries in 1937 which appeared in the *Petroleum Times* (5 March 1938).

	In 1,000 barrels
United States	23,000
Russia	9,200
United Kingdom	3,700
Canada	3,600
Japan	2,500
France	2,300
Germany	1,300
British India	1,050
Italy	900
Australia	450
Belgium	430
Sweden	400
The Netherlands	400
Denmark	350
Iran	320
Argentina	300
Poland	300
Czechoslovakia	270
Union of South Africa	260
Brazil	250
Austria	160
Norway	150
Switzerland	150
Finland	110

The muddled world affairs will probably make their impact upon the consumption of lubricants during the war years.

CHAPTER II

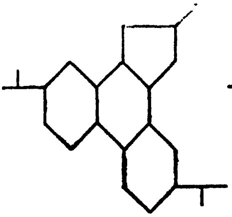
REFINING

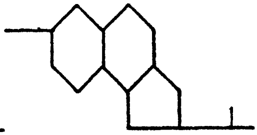
The word petroleum is almost like the heading to a catalogue of gases, anæsthetics, spirits, petrols, illuminants, fuels, lubricants, waxes, jellies, bitumens, asphalts, carbons, and the hundred and one individual products. Such a list makes the subject of petroleum refining look gigantic and complex. It probably is, but to the petroleum industry it is reasonably simple, because it is all worked out on a plan carefully conceived. Refining is perhaps not quite the proper word; perhaps it would be better to use the word resolving. Throughout the whole of the petroleum industry it is the aim to resolve the natural products into marketable fractions. Natural gas used to be burned or allowed to escape into the air, now it is resolved into methane, ethane, ethylene, propylene, and all the other gases which can be used either alone or be converted into other organic compounds. These gases are valuable raw materials for the economic manufacture of alcohols and a wide range of solvents, and even 100 octane motor spirit.

By the well-known processes of distillation, now brought very well up to date on a sound scientific foundation, crude petroleum is resolved into a number of fractions, consisting roughly of petrols, kerosines and lubricants. Each of these main distillates is subdivided according to demand. Then they are refined. Refining consists of the elimination of the unwanted or undesirable constituents from any one particular sub-division. The removal of an undesirable constituent does not necessarily involve its destruction, for that might be wanton waste. What might be undesirable to one marketable commodity might be a valuable raw material for an organic synthesis. The olefines and diolefines were regarded as undesirable gum producers in petrol, but in the future we may see them transformed into motor-car tyres.

The lubricating oil fraction is resolved by distillation into a series of sub-fractions. The object of the resolution is to obtain oils of different viscosities. As the crude oils differ considerably in different localities, so the fractional distillation is varied to meet the constituent members of the crude. The Penna oils are not usually divided into as many fractions as the Californian oils, nor is the distillation carried to give such high viscosity distillates. After the distillates have been removed, there remain the residual stocks, consisting of steam cylinder oils and petrolatums. Distillation of petroleum is perhaps a wrong description; it is probably better to call it fractional condensation. The old system was true distillation from stills or retorts, but now heated oil is conducted into the base of a tower, where it vaporises, ascends, and condenses at various levels, according to the boiling-point of the hydrocarbons. By suitable take-off points fractions can be collected. Distillations are often conducted on such gigantic scales that what appears to be simplicity is in fact very involved.

The exact structure of lubricating oil fractions is not fully known, because the large number of compounds present, as well as their complexity, has so far made accurate chemical analysis impossible.


(1)


(2)


(3)


(4)

We know, with a reasonable degree of certainty, that we are dealing with the general type of chemical structures indicated schematically Hydrocarbons (1) consisting of condensed rings with short branched chains have very low viscosity index. The most highly condensed compounds, which are particularly deficient in hydrogen, are of an asphaltic nature. Hydrocarbons (2) are characterised by a less condensed nucleus with long preponderately straight chains, and have a high viscosity index. In either case the rings may be aromatic or naphthenic, or probably a combination of both. The long chain shown in (3) indicates a high degree of paraffinicity or waxy structure which makes for a very high viscosity index. The moderately branched chains of (4) are intermediate between (2) and (3). Compounds falling in these four classes are found in all lubricating oil fractions, but the extent varies greatly, and makes for marked differences in the viscosity index of oils from different crudes.

CONVENTIONAL REFINING

Refining of lubricating oils includes separating the different types of hydrocarbons according to the viscosity index required, and the removal of wax, asphaltic materials, and sulphur compounds. The so-called conventional method consists of treating the oil with sulphuric acid, washing with caustic soda, and filtering with clay. Much has been written about sulphuric acid refining, but as it is rapidly being replaced by solvent refining, it can be passed over with little notice. By this it should not be imagined that sulphuric acid is being entirely suspended. When refining to obtain a pale colour or white oil, it costs less to use sulphuric acid than a solvent. Cable oils which require stability and low viscosity index are usually acid refined, because solvent treatment would confer an undesirable improvement in viscosity index. Acid refining has been severely criticised on the grounds that it is complicated, extravagant, and produces acid sludge which has a nuisance value. It may leave in the oil sulphonates, polymers, condensation products, and indeed many conversion products.

SOLVENT REFINING

Acid refining has given place largely to solvent refining. This new tool in the petroleum industry separates the hydrocarbons according to solubility, and not by chemical change or reactivity. By removal of the solvent from the soluble fraction unchanged hydrocarbons are obtained. The method seems to be most attractive. Kalichevsky, Simpson and Story (*Oil Gas J.*, 36, 38, 1937) give comparative data between acid refined and solvent refined oils to show the advantages of solvent refining.

	1932 Acid Refined		1937 Solvent Refined	
	S.A.E. 40	S.A.E. 60	S.A.E. 40	S.A.E. 60
Pour Point . .	20°F.	25	0°F.	5°F.
Flash Point . .	430°	480°	460°	515°
Vis. (Saybolt) 100° F.	770″	1765″	660″	1437″
,, ,, 210°F.	73″	110″	73″	110″
Vis. Index . .	83	80	100	98
Carbon residue .	0·9	1·4	0·2	0·3
Sligh Oxidation .	17	4	0	0

Solvent refining dates its origin at the time when Edeleanu was conducting his researches on the cause of smoke when kerosine was burned in lamps. He found that when the kerosine was washed with liquid sulphur dioxide it extracted certain constituents which gave infinitely more smoke than the untreated kerosine, and the insoluble portion burned with much less smoke. This far-reaching discovery enabled Edeleanu to obtain British Patent No. 11,140 in May 1908. Needless to say, the laboratory experiments were quickly followed by large-scale operation.

The investigation was extended by other workers to the field of lubricating oils. A formidable hurdle in the investigation was raised by the fact that sulphur dioxide is a gas at atmospheric temperature and pressure. In order, therefore, to liquefy the gas, the temperature had to be reduced or the pressure raised, or both. Such conditions complicate the large-scale refining plant considerably. Nevertheless, success rewarded the efforts, and large-scale plant has been installed and worked satisfactorily.

The idea of solvent extraction was attractive, and soon the scheme was being tried with many organic liquids, but only a few have been applied. The first solvent extraction plant for lubricating oil was erected in 1927 at the works of the Associated Oil Company, California. In 1930 it would have been difficult to acquire any large quantity of solvent refined oil, but since that date much progress has been made. Obviously it was necessary to turn to those organic liquids which would dissolve selectively the constituents of the oil which were the cause of objectionable features. The property of all satisfactory selective solvents is a separation into two liquid phases. This does not mean that the two layers shall separate like ether from water, merely because the two liquids are virtually insoluble in each other. If the extracting solvent were to be completely insoluble in one layer, extraction would be difficult owing to its inability to permeate the mass and exercise its selective capacity on the soluble portion. It must, however, be sufficiently insoluble to separate and carry with it the extract. The solvent phase is called the extract, and the oil phase the raffinate. The solvent is eventually removed by distillation.

The first method was to contact the solvent and oil in a container fitted with an agitator. The two phases were then separated by settling. Then came the process of bringing the two liquids together in series. The once-treated oil was passed to another tank and re-treated with more solvent. The washing was repeated until the desired result was obtained. Counter-current washing is now the method widely adopted. In principle it consists of passing oil through the solvent extracting plant in one direction, and the solvent in the opposite direction. The two products are intimately mixed whilst flowing in opposite directions. The oil as it passes along meets progressively purer solvent. The degree of refining can be accurately controlled by the proportion of solvent used and the temperature of operation.

After solvent treatment it is frequently found necessary to give the raffinate a light sulphuric acid wash, followed by clay treatment. This depends entirely upon the final utility of the oil. There is an inclination to focus attention upon motor oils and to generalise upon them, and extend the treatment given to them to all lubricating oils, irrespective of their practical applications. Acid and solvent refining may vary, depending upon the refining required and the properties to be achieved.

Very broadly, solvent refining consists of separating paraffinic hydrocarbons from naphthenic hydrocarbons. This statement should not be taken too literally, but in the main it is substantially true. It must be extended to aromatic compounds, asphaltic bodies, sulphur compounds, and wax. Consequently, in solvent refining there must be provision made, when necessary, for de-waxing and de-asphaltising. This may introduce a double solvent treatment.

The lubricating oil distillates containing wax were formerly cooled with or without naphtha, and the crystallised wax filtered off in filter presses. Now the wax is removed with the aid of solvents such as acetone, propane, or benzol-acetone, and the centrifuge. Attention is given to rate of cooling to adjust crystal size, and to the addition of filter aids. These may consist of clays, lampblack, ground grain bulbs, cellular materials, etc. Paraffin wax as we see it in commerce is not the only waxy material which troubles the refiner. The wax of commerce is obtained from the low viscosity distillates, and sweating the pressed wax free from oil. Slop wax which is present in high viscosity oils is usually considered to be unpressable, and the third type is petrolatum or jelly, exists in cylinder stock. Petrolatum is amorphous, and is believed to differ from crystalline wax because of the presence of inhibitors. Slop wax is intermediate between the two. Ceresins are not strictly classified with waxes, as they belong to a family of much higher molecular weight.

When propane is used, oil is blended with 2–3 volumes, and a pressure of 180–200 lb. per square inch is maintained to ensure fluidity at 90–100°F. The pressure is then released and cooling occurs by evaporation, the wax crystallises and is filtered off. Some refiners prefer to use high boiling-point solvents such as benzol-acetone or methyl ethyl ketone. It is a little difficult to be too specific about the selectivity of solvents, because they may exercise extended activities. Propane is used for de-waxing, but it is also valuable for de-asphaltising.

As the composition of asphaltic substances is not known, it is convenient to divide them into groups based upon their carbon hydrogen ratio.

Carboids —insoluble in all organic solvents.
Carbenes —insoluble in benzene, but soluble in carbon disulphide.
Asphaltenes—insoluble in petroleum ether, but soluble in benzene.
Resins —soluble in petroleum ether, but absorbed by clay.

Asphaltenes and resins are mainly found in crude oils. They are usually present as colloids. The resins act as protective colloids, When asphaltenes are freed from resins they are incapable of being dispersed, even in kerosine. By diluting mineral oil with light petroleum solvents the resins lose their protective properties towards asphaltenes, depending upon the decrease in molecular weight of solvent and the degree of dilution. When asphaltenes are removed from oil the viscosity is reduced, due to the reduction of the high molecular weight constituent. It is now easy to visualise how oil is de-asphaltised by clay and solvents. The efficiency of clay seems to be at its best when the oil is at 160–170° F.

It is well known that Penna oils contain a high proportion of high viscosity index constituents, Mid-Continent oils a medium proportion, and Coastal oils a low proportion; consequently, if it is the aim to obtain high viscosity index oils, it will be reasonable to start with Penna oils; on the other hand, if low viscosity index oils are required, consideration should be given to Coastal oils. Selection of stock and choice of solvent are both controlled by the ultimate goal to be achieved. Although in general the raffinate is paraffinic and the extract naphthenic, let it not be believed that all the constituents of a given viscosity index oil are identical, irrespective of the type of crude. Many people have the erroneous idea that solvent refining eliminates all the differences between crudes, and produces single type oils. It does not. Whatever the tendency might be, economics intervene and finally take control.

There is no rule, but it may interest readers to know that sulphur dioxide-benzene is often used for the manufacture of turbine and transformer oils; chlorex ($\beta^1\beta^1$ dichloroethyl ether $CH_2Cl.CH_2{-}O{-}CH_2.CH_2Cl$) is most suitable for paraffinic oils; furfural (furfuraldehyde $C_4H_3O.CHO$) is used for Mid-Continent and Coastal oils; nitrobenzene for Penna oils, and Duo-Sol (propane and cresylic acid) has a wide range of application.

PLANTS IN WORLD, 1937

	barrels per day
Duo-Sol	17,612
Furfural	15,810
Phenol	16,300
Chlorex	6,150
$SO_2-C_6H_6$	2,650
Nitrobenzene	2,500
Nitrobenzene + H_2SO_4	800
	61,822

CHAPTER III

FATTY OILS AND ACIDS

The use of fatty oils does not perhaps date back quite so far as petroleum, but when we consider that petroleum was more accessible in far-distant days than were fatty oils, it is very creditable to learn from the Psalmist that oil was extracted in his day by man "to make him of a cheerful countenance." It is believed that oil was used for barter as well as for external application. There appears to be little doubt that the only fatty oil used was of vegetable origin, but it is uncertain whether it was or was not olive oil. The value of oil as a foodstuff was recognised by the ancients, therefore it became an established industry, but few records are available to mark its progress until its establishment in Holland and the introduction of mills in England in the fifteenth century. The first authentic documentary records of any factory date back to the seventeenth century, and relate to a business at Evesham.

The principle involved in the extraction of oil is the same to-day as it was before the Christian era, namely, the expression of the oil from the fruit by pressure. Vitruvius gave details of a press-room in the year 30 B.C., and Pliny made reference to it in A.D. 77, and later we find the growth of the industry in Holland. Pascal, in 1652, was instrumental in the foundation of the hydraulic press, but it was not until 1795 that the use of water was developed by Bramah, and perfected by Chambauvet in 1830. A few years later Falquire made a press developing 2,987 lb. per sq. in. Of course higher pressures are used to-day. The seed may be crushed cold, as for the manufacture of pharmaceutical castor oil, or hot, as for firsts castor. Sometimes the oil is extracted with solvents, which are subsequently distilled off.

Animal and fish oils are usually extracted by boiling the tissue depot in water. The separated oil is treated with caustic soda, to remove free fatty acids, filtered with fuller's earth to clarify it, and perhaps subjected to the action of superheated steam to deodorise it. The oil may be treated with hydrogen in the presence of a catalyst, to convert it into a hardened or hydrogenated fat.

Most of the oil-producing plants come from tropical countries—palm and palm kernel from Africa, coconut from many of the islands in the Pacific and Indian Oceans, olive from the Mediterranean countries, castor from India and South America, ravison from Southern Russia, rape from East Indies, cottonseed from United States, India or Egypt.

Fatty oils are still used extensively in lubricants. It is difficult to obtain reliable data on the quantities used, or even to give anything more than a very rough estimate. The type of trade of the individual lubricant manufacturer varies so much that any average would be misleading. A company with an all-round business may use a total of 3 per cent of the mineral oil it sells. A large sale of marine engine oils may raise the proportion to 17 per cent. Should soluble oils be the main business, it may be still higher. So when one hears excited arguments about the relative lubricating values of mineral and fatty oils, it is prudent to ascertain which type of business each debater enjoys. Whatever the scientific support may be for either side, the fact still remains that about 20,000 tons of fatty oils are used by the lubricating oil trade in England. The variety of oils used in this industry can, in times of emergency, be reduced to very few, but in times of plenty the list may be extended to about twenty if the requirements of the grease trade are included.

Without doubt, rape oil is the most extensively used. About 5,000 tons per annum may be considered to be a fair estimate. Fish oils are an easy second, with a consumption of about 4,000 tons. In addition to fatty oils, must be considered the large quantity of fatty acids which are used in grease-making.

There is probably nothing seriously wrong with the fatty oils which are in general use, because they have withstood the test of time. New applications are constantly occurring, often quite dissimilar from any other system. What is to be the criterion in such cases? Often a shrewd guess and deduction from experience may suffice. The time has now arrived when past experience must be supplemented with a scientific knowledge of the composition of fats.

Fats and oils are more complex than is generally realised, not only with respect to the multiplicity and variation in types of materials present, but also in the nature of the dominant group of compounds—the fatty acid glycerides. The molecular structure of fats and oils is very fragmentary. The time has come when we have got to get away from the elementary concept of glycerol and three fatty acids. Although the quantities of oils and fats that enter into commercial usage are impressive, we know little about the many phases of their molecular structure, chemical synthesis and breakdown. A knowledge of the composition of natural fats in terms of constituent acids and glycerides is desirable for their intelligent use. In many cases the identification and estimation of the fatty acids is possible, but only in relatively few fats have the component glycerides been studied, owing to their structural peculiarities.

The simple study of the constituent fatty acids in a fat does not give a true picture of its physical properties. Cacao butter, for example, has the same fatty acids in approximately the same amounts as mutton tallow, yet cacao butter is almost like a wax, and mutton tallow is greasy. The difference is due to the oleo distearin and oleo dipalmitin and the negligible quantities of fully saturated glycerides in cacao butter.

	Cacao Butter Per cent	Mutton Tallow Per cent
Fatty acids:		
Myristic	0·0	4·6
Palmitic	24·4	24·7
Stearic	34·5	30·4
Oleic	39·1	36·0
Linoleic	2·0	4·3
Glyceride:		
Fully saturated . . .	2·5	26
Mono-unsat, di-sat. . .	77	30–52
Di-unsat, mono-sat. . .	16	44–0
Tri-unsat.	4	0–22
Melting-point . . .	34° C.	44–49° C.

Marine mammals such as seal, whale or porpoise and dolphin possess a layer of fatty tissue beneath the skin known as blubber, from which oil is extracted. The sperm whale yields oil also from the head cavity. These oils differ considerably in composition, and are of considerable interest in lubrication. The fatty acid contents reveal fundamental differences.

There does not appear to be any published analysis of the fatty acids of seal oil which would assist in the present comparison. The principal characteristic of whale oil is the high percentage of the higher unsaturated fatty acids. Generally, the iodine value of the

	Saturated					Unsaturated				
	C_5	C_{12}	C_{14}	C_{16}	C_{18}	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}
Whale										
Arctic	—	—	4·1	10·6	3·5	—	18·4 (−2H)	32·8 (−3H)	19·3 (−7H)	11·3 (−8H)
Antarctic	—	—	6·3	18·2	2·4	3·7 (−2H)	13·3 (−2H)	38·4 (−2·6H)	11·4 (−5·6H)	6·3 (−9H)
Sperm										
Head	—	16	14	8	2	14 (−2H)	15 (−2H)	17 (−2H)	6·5 (−2H)	—
Blubber	—	1	5	6·5	—	4 (−2H)	26·5 (−2H)	37 (−2H)	19 (−2·5H)	1 (−4H)
Porpoise										
Head	13·9	2·4	12·5	11·6	0·4	2·7 (−2H)	25·4 (−2H)	15·8 (−2·8H)	12·7 (−5·5H)	2·6 (−7·2H)
Body	3·2	1·0	7·2	8·6	0·8	4·7 (−2H)	25·9 (−2H)	24·1 (−3·3H)	18·6 (−6·5H)	5·9 (−7·6H)

oil from the Antarctic whale is lower than that from the Arctic whale, which is in accordance with the component fatty acids. Whale oil is regarded as a cheaper alternative to rape in lubricants, consequently, a preference would normally be given to the whale oil with the lower iodine value, if there were an opportunity to make a selection. Sperm oil is entirely different from whale oil. Sperm oil is a liquid wax in which the fatty acids are combined with the higher aliphatic alcohols. An oil is essentially a combination of fatty acids with a trihydric alcohol (glycerol), and in a wax with monohydric alcohols. The fatty acids in sperm oil are more saturated than in whale, and the unsaturated acids are mainly mono-ethenoid. This, of course, accounts for the substantially lower iodine value. The peculiar composition must confer upon it singular properties. Just what they are has never been concisely defined, but it is often spoken of as a nice clean oil. Loose though the expression may be, it conveys a time-honoured flavour, and an incentive to further study. In the past it was used for spindle lubrication in the textile mills, possibly because of its low viscosity, and perhaps because of the ease with which it could be removed from the fibre or yarn. Doubtless a closer study will lead to a reward commercially. The outstanding feature of porpoise oil is the presence of isovaleric acid $(CH_3)_2CH.CH_2COOH$, and of higher aliphatic alcohols in addition to glycerides. The high proportion of saturated acids in the head oil has made it particularly valuable for the lubrication of fine instruments.

In the past our limited knowledge has led us to picture fats as a simple mixture of triglycerides, such as triolein, tripalmitin, etc. Now it is known that the existence of such simple glycerides is the exception. The manner in which the component fatty acids are combined with the glycerol leads to the formation of complex glycerides. The differences between fats is not only due to the component acids, but to the actual glycerides, as was shown in cacao butter and mutton tallow.

Castor oil is unique in its high content of ricinoleic acid, $CH_3 \cdot (CH_2)_5 CH(OH) \cdot CH_2 \cdot CH{:}CH(CH_2)_7 \cdot COOH$, and its almost complete absence of any palmitic or other saturated acids. This acid was thought to exist in grape seed oil, but later work has shown that the acetyl value was due to some of the glycerides which had become hydrolysed. The only other oil known to contain this acid is ivory wood oil (*Agonandra brasiliensis*). Castor oil stands out from all others in several ways. It has an exceptionally high viscosity, low coefficient of friction, high efficiency for gear lubrication, and its solubility in mineral oil is only 1 or 2 per cent. These characteristics are no doubt largely traceable to the presence of the hydroxyl group.

Citicia oil contains licanic acid, $CH_3 \cdot (CH_2)_3 \cdot CH{:}CH \cdot CH{:}CH \cdot CH{:}CH \cdot (CH_2)_4 \cdot CO \cdot (CH_2)_2 . COOH$. The presence of the ketone group makes it interesting, but the triethenoid structure precludes its use from lubrication. Another oil which is distinctive is chaulmoogra. It contains chaulmoogric acid characterised by a cyclopentene group. Probably this structure accounts for its efficiency in the treatment of leprosy.

The fatty acids from the seeds of *Picramnia Sow* found in Central America consist of nearly 95 per cent of tariric acid, $CH_3 \cdot (CH_2)_{10} \cdot C \vdots C \cdot (CH_2)_4 \cdot COOH$. The occurrence of this acetylenic acid is at present confined to this one Central American genus.

Mustard, rape, ravison and wallflower seed oils all contain a large amount of erucic acid, $CH_3 \cdot (CH_2)_7 \cdot CH{:}CH \cdot (CH_2)_{11} \cdot COOH$, and only a negligible quantity of saturated acids. Indian rape oil is used very extensively in lubrication; therefore it is useful to compare the acid contents with those in the English and German-grown seeds. From the point of view of unsaturation the Indian oil is substantially the best. Ravison oil is used as a substitute for rape, but it is inferior to the German rape. As an alternative to Indian rape, consideration should be given to white mustard and English rape, both of which can be grown in this country.

The high percentage of the tri-ethenoid linolenic acid

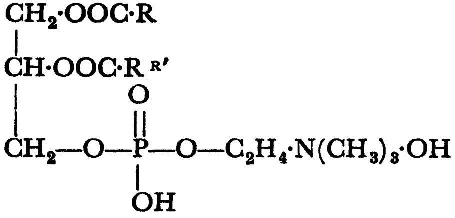
	Saturated				
	Myristic C_{14}	Palmitic C_{16}	Stearic C_{18}	Arachidic C_{20}	Ligroceric C_{24}
White mustard	—	—	—	—	—
Rape, Indian	—	—	—	—	—
„ English	—	under 2		—	—
„ German	—			—	—
Ravison	—			—	—
Wallflower	—			—	—
Linseed	—	8·9		—	—
Cottonseed	0·3	19·1	1·9	0·6	—
Indian oak (acorn)	—	17·1	—	—	—
Horse chestnut	—	4·4	3·6	—	—
Olive	—	6·0	4·0	—	—
Sesame	—	9·1	4·3	—	—
Soybean	—	6·5	4·2	0·7	0·1
Sunflower	—	1·5	7·0	—	—

	Unsaturated			
	Oleic C_{18} mono-ethenoid	Linoleic C_{18} di-ethenoid	Linolenic C_{18} tri-ethenoid	Erucic C_{22} mono-ethenoid
White mustard	28	14·5	1	52·5
Rape, Indian	20·2	14·5	2·1	57·2
„ English	32	15	1	50
„ German	39·3	11	3·7	45·2
Ravison	20·5	25·5	2	47·5
Wallflower	12	42	4	38·5
Linseed	18·8	23·2	49·1	—
Cottonseed	33·1	39·4	—	—
Indian oak (acorn)	82	—	—	—
Horse chestnut	67·1	22·7	2·2	—
Olive	83	7	—	—
Sesame	45·4	40·4	—	—
Soybean	32	49·3	2·2	—
Sunflower	26·7	64·8	—	—

$CH_3\cdot(CH_2)_4\cdot CH{:}CH\cdot CH_2\cdot CH{:}CH\cdot CH_2\cdot CH{:}CH\cdot(CH_2)_4\cdot COOH$, in linseed oil accounts for its drying properties, and use in paints.

The remainder of the oils recorded in this table contain significant quantities of saturated acids which are likely to be deposited in cold weather, a factor to be considered in lubrication. One advantage of rape oil is its ability to remain fluid at low temperatures. Olive oil was much favoured years ago, leaving in its wake a few adherents. About 1935 the olive growers tried hard to re-establish it, but the war frustrated their plans, except perhaps in countries where mineral and other oils are scarce. Should olive oil be restored to favour, it would be prudent to turn attention to the Indian oak acorn. In this country we might find use for oil from the horse chestnut. The figures for sunflower oil are given to show that this home-produced material could not be used in lubrication. The presence of phosphatides in soya bean is worthy of special mention.

Lecithin is the common phosphatide of commerce. It consists of two fatty acid radicals esterified to glycerol, and a phosphoric acid radical attached to a nitrogenous base group choline.



$$\begin{array}{l} CH_2\cdot OOC\cdot R \\ | \\ CH\cdot OOC\cdot R\ {}^{R'} \\ |\qquad\quad O \\ |\qquad\quad \| \\ CH_2—O—P—O—C_2H_4\cdot N(CH_3)_3\cdot OH \\ \qquad\quad\ | \\ \qquad\quad\ OH \end{array}$$

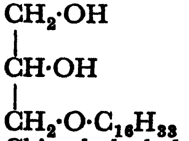
	Saturated			Unsaturated		
	Myristic C_{14}	Palmitic C_{16}	Stearic C_{18}	Oleic C_{18}	Linoleic C_{18}	Linolenic C_{18}
Horse .	—	29	7	55	7	2
Neatsfoot .	—	18	3	79	—	—
Bone fat .	—	20	20	52	8	—
Mutton tallow .	1	21	30	43	5	—
Beef tallow.	4·5	30·6	19·2	42·7	3	—
Lard . .	1·0	28	12	48	6	—

Linoleic acid in these animal fats is not identical with that combined in vegetable oils. The figures given must be taken as representative because diet has an influence upon ultimate composition. These animal fats contain mainly palmitic, stearic and oleic acids. The liquid character of neatsfoot would be expected from its high percentage of oleic acid. Its content of palmitic acid is readily removed by freezing out.

	Saturated								Unsaturated	
	C_8	C_{10}	C_{12}	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}	Oleic	Linoleic
Groundnut . . .	—	—	—	—	6·3	4·9	5·9	5·9	61·1	21·8
Coconut . . .	9·5	4·5	51	18·5	7·5	3·0	—	—	5·0	1·0
Palm Kernel . .	13·0	3·0	52	15	7·5	2·5	—	—	16	1·0

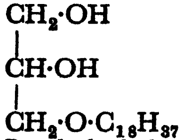
Although these three fats are of interest in the food industries, groundnut and coconut were used prior to 1939 in lubrication. For a long period coconut oil was used in compounding gas and petrol engine oils. Outside bulk storage at garages tended to cause precipitation of saturated glycerides, of which there is a preponderance, in cold weather. The separation does not occur so readily in small containers. Groundnut oil has not reached expectations, probably because the linoleic acid content has led to gumming.

Waxes in general are not used in lubrication; consequently, the monohydric alcohols present in them are outside the scope of this book. The alcohol which is found in sperm oil and porpoise oil is mainly oleyl alcohol. Oleyl alcohol may roughly be regarded as the unsaturated edition of cetyl alcohol from spermaceti, which is the solid wax present in the head of the sperm whale. There is a bridge between the alcohols and glycerol. In the liver oil from the ratfish, caught off the coast between California and Alaska, there is about 30 per cent of unsaponifiables consisting of glycerol ethers.



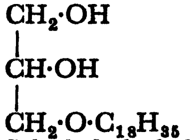
$$\begin{array}{l} CH_2\cdot OH \\ | \\ CH\cdot OH \\ | \\ CH_2\cdot O\cdot C_{16}H_{33} \end{array}$$

Chimyl alcohol
M.P. 61°C.



$$\begin{array}{l} CH_2\cdot OH \\ | \\ CH\cdot OH \\ | \\ CH_2\cdot O\cdot C_{18}H_{37} \end{array}$$

Batyl alcohol
M.P. 70°C.



$$\begin{array}{l} CH_2\cdot OH \\ | \\ CH\cdot OH \\ | \\ CH_2\cdot O\cdot C_{18}H_{35} \end{array}$$

Selachyl alcohol
Liquid

Naphthenic Acids

Naphthenic acids do not belong to the domain of fatty oils, but as they are utilised in lubrication, they come within the purview of this book.

True naphthenic acids are probably normal constituents of all crude mineral oils to the extent of 0·03–8·0 per cent, but their potential annual production of 50,000 tons would be difficult to attain, owing to practical difficulties. They are usually recovered as sodium naphthenates from these sources.

1. Crude oil or straight-run distillate is distilled from sodium hydroxide, leaving a residue of resins, asphalt, oil and sodium naphthenate.
2. Distillates of gas oil and kerosine type are extracted with an aqueous solution of sodium hydroxide.
3. From soda sludge, which is obtained by neutralising the residual acidity in a sulphuric acid treated oil after the acid sludge has been separated. The true naphthenic acids remain unsulphonated during the acid treatment of the oil.

The naphthenic acids can be isolated from:

(1) By diluting with oil or kerosine and extracting the sodium naphthenates by discharging the hot solution on to flowing water. The acids are liberated by sulphuric acid.

(2) By extracting the residue with ethyl alcohol in which the sodium naphthenates are soluble.

(3) By acidification, oils, etc., are liberated. The naphthenic acids can then be separated by distillation after mixing with oil whose boiling-point is below that of the asphalt. Oil is added as a carrier liquid to facilitate distillation.

The separated acids are impure, but by distillation a purity of about 93 per cent. can be obtained. Should a greater purity be desired, other methods of refining must be adopted. One method consists of distilling the acids over copper oxides. Treatment with sulphuric acid was formerly thought to sulphonate the naphthenic acids, but now it is held to be a precipitant of impurities. When it is used, attention must be given to the strength and quantity of the acid.

Various formulae have been suggested for naphthenic acids on rather slender evidence. Whilst the general formulae of the order of $C_nH_{2n-2}\cdot COOH$ and $C_nH_{2n-4}\cdot COOH$ are recognised, it would be difficult to go further than saying that they are derivatives of cyclopentane acids.

Efforts have been made to identify and locate the substituents in the cyclopentane ring, and the number of carbon atoms between the carboxyl group and the ring.

Naphthenic acids are in limited competition with fatty acids from glycerides. How far the competition will grow is difficult to forecast, owing to the chemical and physical differences between them. For the paint industry they are converted into heavy metal soaps, to serve as driers. They are also used in the manufacture of anti-fouling compositions for ships' bottoms. Sodium soaps of fatty acids have a characteristic difference from sodium naphthenates. Sodium soaps even in low concentrations in water give rise to a gel, whereas concentrations up to 50 per cent of sodium naphthenates in water flow freely. For the manufacture of soluble oil this characteristic of sodium naphthenate is particularly useful. So far as the author is aware, they are not entirely successful for this purpose unless a coupling agent is incorporated. The emulsifying power of them makes them useful in many directions. As a lubricant, sodium naphthenate has been incorporated with petroleum to form a grease. Aluminium naphthenate, with a small quantity of sodium naphthenate, will dissolve in oil to give a transparent lubricant. Such a lubricant has been sold as castor machine oil.

PETROLEUM SULPHONATES

Sulpho acids or petroleum sulphonates are obtained from petroleum by treatment with sulphuric acid. In refining petroleum oils, strong sulphuric acid is added to remove impurities such as asphaltenes and sulphur compounds. From the acid sludge which forms, green acids are separated by diluting with water in sufficient quantity to give a 50 per cent acid concentration. In this strength sulphuric acid the green acids are in minimum solubility. On separation, they can be used in the impure state for certain purposes, such as emulsifiers. If necessary, they can be split into groups of high and low molecular weights. The low molecular weight acids form water insoluble salts. The green acids have a molecular weight range of 150–1,000. They are quantitatively precipitated from adilute acid solution by fresh albumen or by ethyl benzylaniline.

By subsequent treatment with sulphuric acid in the manufacture of white oils, sulpho acids are produced which are soluble in the oil. These acids are extracted with alcohol. Commercially they are known as mahogany acids or petroleum sulphonates. The old name sulpho-naphthenates is going out of favour, because it is now believed that they are not sulphonated naphthenic acids. On neutralising with sodium hydroxide, they form salts which are soluble both in water and oil. For this reason the salts are employed extensively in the manufacture of soluble oils. Further purification can be effected by extraction with petroleum spirit. The heavy metal salts have found a limited use as detergents in diesel lubricating oil.

An approximate estimation of the petroleum sulphonates can be done by extracting with 50 per cent alcohol and washing with petroleum spirit. The free acids can be separated from the sodium salt by washing repeatedly an ether solution with strong hydrochloric acid.

CHAPTER IV

ADDITIVES

THE practice of using thickeners for anything but a legitimate purpose has practically passed into oblivion, but the impartation of an abnormal viscosity is practised for a specific purpose. The wide range of petroleum products from spindle to steam cylinder oils reduces the need for searching for viscosity increasers. Considerations of temperature may limit the application of pure petroleum products, in which event modifications become imperative. Blending oil with soaps to form grease is, basically, a thickening of oil to meet a definite requirement. The addition of soaps is widely practised. Indeed, any oil blended with a soap is crudely designated a grease. The description is a little misleading, because of the demand for what are sometimes called liquid greases. No objection can be raised against the term if it provides a means of describing them or differentiating from other things. Liquid greases have found favour in the textile industry as lubricants in small gear boxes operating on machines where oil leakage would be detrimental to the yarn or fabric. A small quantity of soap will increase the viscosity of the oil, and form a structure, which reduces the risk of leakage beyond that which would occur with a pure oil. Larger quantities of soap give rise to the soft greases, such as are used in high pressure greasing plants installed in garages. The long lengths of feed piping necessitates a soft grease to obviate high propelling forces. The ordinary greases of commerce owe their consistencies to the varying amounts of soaps present.

Calcium and sodium soaps are the principal ones used, but aluminium and lead soaps have their special uses. Calcium and sodium soap greases can roughly be characterised by their melting-points. Lime soap greases melt up to 220° F., and soda greases up to their decomposition temperature. Aluminium soap greases are still the speciality of a few manufacturers, due to the technique required in their manufacture. Lead soap greases are in little demand, but are useful because the soap is in solution, and the grease melts on heating.

Rubber has a limited range of usefulness, and is therefore hardly worthy of consideration. Rubber latex has attracted attention, but with the introduction of synthetic polymers, like polyisobutene, has faded into the background. The war has given polymers a real start. Low freeze lubricants for the external parts of aircraft has opened the gate for them. Polymers were not exactly a war-time discovery; they were known prior to 1929 as viscosity index improvers. In those days there was a danger that they might be used without discretion, for no other object than to bolster up the viscosity index of a low viscosity index oil. In their proper place viscosity index improvers are excellent, and are to be commended.

The motor-car and the aeroplane have been mainly responsible for the present-day use of additives. In no other class of machinery have demands on the lubricant increased at such a rate as with the internal combustion engine, in its development from Seldon's motor of 1879, or even from the motor of ten years ago, to our present high compression engines.

Refining methods have been improved continuously to keep abreast of requirements. Some crude oils respond to treatment, others are not so responsive. Some produce lubricants which are much sought after for internal combustion engines. Solvent extraction methods have carried the progress a long way, but the demands remain swift and heavy. The object of refining is to remove the undesired constituents which give rise to sludge in the crank case, deposits on the piston head, free organic acids and separation of wax crystals on cooling. Refining can only be carried a certain distance if a satisfactory lubricant is to be achieved. Ultra-refining leads to the white and medicinal paraffins. Whilst it would not be strictly true to say that white paraffins have no place in lubrication, it would be in order to reserve them for very special work.

The modern internal combustion engine demands lubricants of a different type from those which were satisfactory a few years ago. They must be capable of carrying heavier loads, permit easy starting at low temperatures, operating at higher temperatures, and give less solid oxidation products.

Easy starting at all climatic temperatures is a natural demand. Mechanical starting is operated by a big output from the electric battery on the car. In cold weather the stress on the battery is often very detrimental to its life; consequently, something must be done to save it from an early destruction. Further, in very cold weather the battery may be totally incapable of yielding sufficient current to turn the engine sufficiently quickly to effect a start. Slow turning of the engine is useless. Every engine must be rotated above a minimum number of revolutions to suck in sufficient petrol and produce sufficient explosions in a given time to overcome the internal friction of the engine and the oil. As the fluid friction of the oil is the dominant factor, it follows that this must be reduced to a value which is within the power of the battery. This is easily done by using an oil of sufficiently low viscosity at the temperature of starting. Under summer conditions no difficulty is experienced, but in cold weather it is necessary to decide upon the correct viscosity to suit the temperature. Clearly no universal definition is possible, because so much depends upon the capacity of the battery and the starting motor. Much experimental work has been conducted on this important subject in pre-war days, and as one can imagine, intensively during the war. The viscosity of the oil at starting temperature should not exceed 10,000 seconds, though it can exceed this if everything is in its favour. Starting in the winter when the temperature is 32° F., no problem is involved, but at 0° F. some difficulty is encountered without recourse to artificial aid. At this stage it should be made known that when a petroleum oil loses its fluidity at 0° F. or above it is mainly due to the amassing of small crystals of paraffin wax. Pour point depressants have been introduced to change the crystalline structure in such a way that fluidity is maintained at a lower temperature. To meet much lower starting temperatures, it is customary to dilute the lubricating oil with suitable kerosine.

When an oil is in circulation in an engine it is in intimate association with oxygen both in aeration and solution. At atmospheric temperature there is little temptation for the two to combine, but as the temperature is increased, there is a greater and greater disposition for union to occur. In short, the oil oxidises and gives rise to solid, liquid and gaseous products. The gaseous compounds are of little practical importance as they are lost to atmosphere. The solids have a big nuisance value when they choke the filter, fix the rings, and pile up in the combustion space. A choked filter can cause oil starvation, stuck rings loss of power, and deposits violent knocking. Liquid products contain free fatty acids liable at any moment to enter upon corrosive activity. Oxidation is probably the biggest problem in lubrication, because of its intensive effects. Refining has helped enormously in its reduction, but it has not cured it.

In many industries inhibitors are used to reduce the velocity of reaction. It is not surprising, therefore, that the chemist should suggest inhibitors to give resistance to lubricating oils. Prior to 1935 little was known about the applied use of oil oxidation inhibitors. For low temperature operation β-naphthol, phenyl-α-naphthylamine, and tertiary butyl cresol had been used successfully, but for high temperature conditions much success had not been obtained. Patents had been applied for, and scientific publications made, but it is probably true to say that the introduction of metallic soaps were the first anti-oxidants to be used on a large scale for petrol engine lubrication. The behaviour of metallic soaps had been known some few years previously, but it was not until the surprising effect of a combination of heavy metal soaps had been discovered that they became really useful. A series of engine tests on the bench gave the following results:

				Deposit
Untreated oil				100
Oil +	0·1	per cent	tin oleate	90
,, +	0·2	,,	chromium oleate	78
,, +	0·8	,,	,, ,,	72
,, +	0·1 0·8	,, ,,	tin oleate chromium oleate	58
,, +	0·1 0·4	,, ,,	tin oleate chromium oleate	62

The engine was run under load at a temperature at which the maximum amount of deposit could be produced in the combustion space. The deposit produced by the untreated oil was given the arbitrary value of 100, and the other results were compared with it. The author's explanation of the inhibition is that the soaps do not necessarily check the oxidation of the oil, but rather that they reduce the pro-oxidation of the iron of the engine.[1] Some metals are very strong oxidation promoters, and thereby claim a prominent part in the formation of solid deposits. Copper and iron are specially worthy of mention. It is possible that the ordinary products of oxidation, which themselves give rise to the catalytic nature of the reaction between oil and oxygen, co-ordinate with the metallic accelerator to increase still further the oxidation. This increased oxidation is inhibited by the tin and chromium soaps. At first sight it may appear that such inhibition is small, but when it is realised how much effect the iron has, the surprise must disappear. Whatever doubt there may exist about the theory, the practical results supply the conclusion.

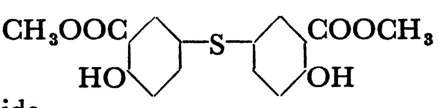
Chromium and tin soaps have been useful in preventing ring sticking in compression ignition engines, probably through their detergent character. This property is not confined to these soaps. Aluminium naphthenate won favour until it was discovered that it led to cylinder wear. Then calcium dichlorostearate was introduced, and was quite satisfactory when white metal bearings were used, but when copper-lead bearings were used, pitting resulted. Later tin and other heavy metals were combined with compounds of high molecular weight. Polysulphides, either alone or in combination with alkaline earth metals, have been used in conjunction with complex esters.

Scuffing, scratching, and wear of cylinders in aero engines, pitting of gears, and pitting of cadmium bearings, became major problems in operational flight in aerial combat. Pitting of bearings was thought to be due to acid corrosion. Whatever the cause may be, it proved to be a difficult problem to stop, because there are so few known substances which are effective. Tributyl phosphite is widely used, and it is known that triphenyl phosphite and mercaptobenzothiazole can be used. The pitting of gears has been considered to be an extreme pressure lubrication problem. Doubtless to some extent it is, but to the author's mind oiliness enters the subject. After the war it will probably be permitted to explain how the difficulty was solved. Cylinder troubles are being dealt with by the use of secret proprietary compounds.

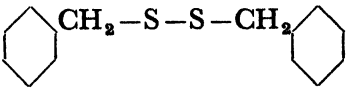
The conception of the hypoid gear, about 1929, resulted in the birth of extreme pressure gear lubricants. Lately these lubricants have been used with advantage in many gear units, excepting worm gears. The rolling and sliding friction in a hypoid gear exert forces which are beyond the power of mineral and fatty oils. For extreme pressure conditions a mineral oil containing one or more chemical additives is used. The function of the additive is not to combine or react with the oil, nor to be adsorbed on the metal surface analogously to a fatty oil. Exactly how it behaves is still unsolved. A working hypothesis has been advanced that its active atoms combine with the metal producing a protective coating. As the popular agents contain sulphur, chlorine or phosphorus, the hypothesis suggests that the film is either a sulphide, chloride or phosphide. Finch has shown by electron diffraction methods that an amorphous oxide film is produced. Whether this is contaminated with the E.P. active agent is not clear.

The early sulphur compounds which were used were sulphurised fatty oils and fatty acids. The increase in tooth loading and shearing forces led to higher operational temperatures, which in turn led to sulphur corrosion. To combat this lead soaps were incorporated into the lubricant. Then came criticisms from the ball bearing makers, who proclaimed that the lead soaps damaged their bearings. The probable explanation was that when the soaps were made by treating lead oxide with fatty acids some oxide remained unconverted to abrade the balls. This problem was faced successfully. Another difficulty which was not so easily solved was the precipitation of lead sulphide through the inter-action of the sulphurised oil and the lead soap. Although the precipitation in any one lubricant may have been cured, it is by no means certain that when two such lubricants are mixed, freedom from trouble is assured. For this reason manufacturers recommend that mixing shall be avoided. The comparative ease with which these lubricants attack metal has earned for them the description "active sulphur lubricants." When used with ferrous metals, a darkening of the metal frequently occurs, but with cuprous alloys black flakes may be formed.

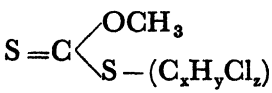
The time came when it was necessary to turn from undefined compounds and direct attention to compounds of more exactly defined constitution. The very large number of patents on the subject is sufficient testimony to the importance of the subject. Should the reader be interested in the details, he is directed to a paper by the author in the *Journal of the Institution of Automobile Engineers*, October 1942. Amongst the sulphur compounds suggested special mention should be made of bis (3-carbomethoxy-4-hydroxyphenyl) thioether



dibenzyl disulphide



and chlorinated alkyl thiocarbonates



$$S=C\begin{cases}OCH_3\\S-(C_xH_yCl_z)\end{cases}$$

Chlorine is represented by chlorinated paraffin wax, and phosphorus by tributyl phosphite. Chlorinated paraffin wax is particularly useful in conjunction with compounds such as thioether or dibenzyl disulphide for hypoid lubricants. The added effect of chlorine can be obtained by incorporating it into the sulphur compound molecule as in chlorinated alkyl thiocarbonates. Phosphorus compounds have not yet been made with a sufficiently high film rupture strength for hypoid gear lubrication.

The use of chemical additives in lubricants has become extremely important, and will be extended considerably when the opportunity for research returns. Students of lubrication are therefore advised to study the subject before it becomes more complicated.

A book on Additives is in the course of preparation by the author.

CHAPTER V

FRICTION AND LUBRICATION

FRICTION is the resistance to motion, and lubrication is the art of reducing it. To the engineer friction is mainly limited to the movement of solids, but he must also be interested in the flow of liquids and gases, or the passage of solids through liquids or gases. Do not let it be supposed, therefore, that lubrication is limited to the reduction of friction between solids. The reduction of friction between solids and gases has interested workers on ballistics and aerodynamics, who so far have devoted their energies to surface form. The flow of water through pipes may have a job of work to do *en route*, consequently a minute quantity of soluble oil is added. Friction between solids can only be reduced by selecting a suitable lubricant. Oil might be suitable for metal, but it would not be the first choice for wood or plastics.

The two theories which have been advanced to explain friction are both tenable. Interlocking of crests and dips seems so obvious that any other explanation seems unnecessary, yet it will be seen that a supplementary thought is desirable. Suppose that two very rough pieces of metal are pressed together, a definite resistance is offered if one is moved over the other. This resistance is simply caused by the interlocking of the crests of one surface with the dips in the other surface. The surfaces can be levelled by filing with a coarse file. If the same procedure is repeated, resistance is again observed. The resistance is again due to the interlocking of the protruding parts into the file cuts on the other surface. Obviously, if these file cuts are smoothed out with a finer file, there still remains unevenness, due to cutting of the surface with the file; thus interlocking would still occur if the metals were passed over each other under pressure. The file marks can still further be removed by very careful grinding; in fact, it is still possible to grind the surfaces to a finish where imperfections can only be seen by the aid of beams of light suitably directed on to its surface.

If friction were purely dependent upon interlocking, friction should vanish if the two surfaces are ground to an optically plain surface. In practice it is impossible to prepare a surface which is perfectly plain. Hence any study of friction cannot be separated from a consideration of surface irregularities.

STICK-SLIP

Bowden, during a period of enforced idleness in the Alps, gave thought to the friction of his skis on the snow. These preliminary ponderings materialised in his work at Cambridge, where he endeavoured to ascertain the total contact area between two very highly polished surfaces of copper, each one foot square. His result may be open to criticism, but it matters little in this illustration, as it was only a fraction of a square millimetre. It seems almost incredible that such a large area is supported upon so small an area. How ridiculous it makes the accepted calculations on bearing areas appear. Still, such calculations are necessary, and will continue to be made. The academic importance is that gigantic intensive pressures are exerted upon pin points.

This observation led Bowden to construct apparatus which would enable him to record rapid fluctuations of friction, should they occur. With this set-up he demonstrated that violent fluctuations do occur. By measuring the temperature simultaneously, he showed that there is a very close correlation between the fluctuations in temperature and the fluctuations in friction. The rise and fall in temperature may be all over in a thousandth of a second. The surface temperature was measured by using the rubbing contact of the two different metals as a thermocouple. By increasing the load, or the speed, the melting-point of the metal could easily be reached. When the melting-point is reached there is no further rise in temperature. The surface temperatures produced by lead sliding on mild steel are indicative of what would happen on a white metal bearing, and what does happen on a copper-lead bearing. The lead melts and spreads over the copper, and even forms a layer on the steel journal. When constantin slides on mild steel, local temperatures of 1,000°C. can be reached on a dry surface, and 500°C. on a lubricated surface.

The recording of friction and temperature shows the fluctuations. The lower recording is an extended section of one fluctuation to prove that when the friction rises to a maximum there is a violent increase in temperature, followed by a sudden drop in friction and temperature. Then the friction rises again with a corresponding temperature increase, and sudden drop. The explanation is that the friction rises and produces heat until the two metal crests melt

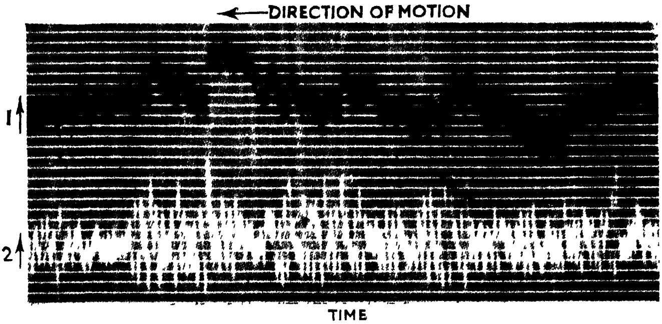


Fig. 1.—The Fluctuating Friction (1) and the Fluctuating Surface Temperature (2) between Steel and Constantan Surfaces.

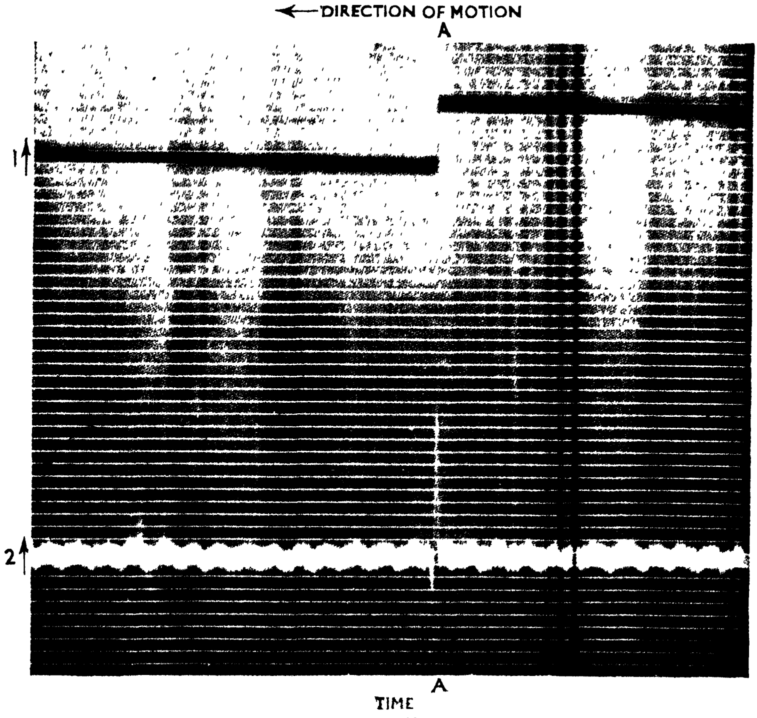


Fig. 2.—Analysis of the effect shown in Fig. 1. (Inst. Mech. Eng. 1937)

and fuse together. Then the weld breaks, the temperature drops, and the cycle commences again. Should we feel disposed to accept this observation as a general phenomenon, then we must acknowledge that friction occurs at the tips of the crests on highly polished surfaces. Clearly such high temperatures can only be obtained when the rubbing surfaces are sufficiently close for contact to occur where the quantity of oil passing must of necessity be small, and the conveyance of heat small. The temperature recorded does not measure the amount of heat, but only its intensity; therefore it is unnecessary to plunge into alarm at the sight of something startling until its significance has been established. If the crests are of micro-dimensions, and the time for one crest to slide over another is less than a thousandth of a second, then the quantity of heat generated, and stored, in the tip of the crest must be almost negligible, and can be ignored. A multiplication of events, however, may very quickly assume important proportions, and instant action must be taken to avoid disaster. So when metal to metal friction occurs continually, and the heat is not dispersed more quickly than it is generated, fusion of the crests is certain, and welding of the opposing surfaces probable. Provided the tiny welds are broken asunder immediately, there will be no general seizure.

This stick-slip theory has created a popular interest, due to its practicability, and supported by easily understood experimental evidence. Care should be exercised to prevent it from being stretched to absurd limits—a fate often accorded to contributions in the less charted seas. The admirable work of Hardy lost some of its glamour because it was not universally realised that his major studies were restricted to static friction. Stick-slip is limited to very near approach, and not to fluid film lubrication. It is capable of expansion to explain several problems. A weld can be such that when fracture occurs the whole crest is removed, leaving behind a crater or pit. A pitted surface is so common that further comment is unnecessary, except to exclude corrosion. When the bearing metal is of comparatively low melting-point it may fuse, weld, and be drawn out to a thread before it fractures.

MOLECULAR ATTRACTION

As all molecules, even those at the surface, are endowed with an attractive force, they have lines of force extending beyond the surface in similar fashion to a magnet, due to the electrically charged electrons and protons. These lines of force have the power to hold fluids or solids with which they come in contact. Although their range is only one to three Ångstrom units (1Å=one ten millionth of a millimetre, 10^{-8} cm.) their affinities are very powerful. The manifestation of this force is only appreciated when the surfaces of metal are sufficiently close to be within the radius of attraction. An effective way of illustrating this is by the well-known experiment of taking a cube of copper with one highly polished surface, and placing it on another similarly polished cube of exactly the same dimensions. The two cubes will adhere to each other by the natural attraction between them. This operation can be repeated eleven times, so that finally there is one cube supporting a chain of eleven others.

It might be argued that the attractive forces are relatively unimportant, because surface irregularities of machinery parts are too great to allow them to operate to the full. The irregularities of an average turned crankpin are of the order of 0·003 mm., whereas on an optically plane surface to one-tenth of a wave length of sodium light the irregularities would be 200 Å units. Furthermore, as it is exceedingly difficult to remove adsorbed layers of contamination from a metal surface, the whole effect of attractive force may be entirely obscured by this thin film. This film may consist of a monomolecular layer which is of the order of 10^{-6} cm., according to Kyropoulos (*General Discussion on Lubrication*, 1937). Hence a monomolecular film of oil is greater than the radius of attraction of surface molecules. The chief interest of surface attraction lies in its ability to attract and hold a film of lubricant. In view of the work of Bowden, it may not be necessary to consider any alliance between molecular attraction and seizure, but to concentrate upon surface irregularities and the fusion of the crests giving rise to minute bridges. Adam (*General Discussion*, 1937) suggests that the speed of formation of the locally welded bridges is surprising. If the surface of one metal slides over another metal at a speed of 100 cm. per second, and the bridges are 0·1 mm. across, the time of contact at any one point must be of the order of 10^{-4} seconds, during which the bridge is formed and broken.

RUNNING-IN

After a machine is made, the first operation is to run it in to enable it to work smoothly. The amount of running-in which is necessary depends upon the finish on the surfaces. Formerly it was assumed that running-in reduced the crests by wear, and finally produced a smooth surface. That hypothesis has somewhat changed during recent years. Now it is conceivable that the tips of the crests are melted, and the minute particle of molten metal flows down the slope, where it freezes. Electron diffraction, a new and powerful means for the study of surface structure, has been applied by Finch to wear and lubrication. He has revealed facts of outstanding importance. Cutting or abrasive methods of smoothing a metal surface leave its structure crystalline. The surface finish put on a metal by hammering, burnishing and polishing is quite different in its structure from that afforded by abrasive methods. The surface is not abraded, but smoothed to a state of high finish by a smearing over the surface of molten or viscous material formed at the crests as a result of high temperature. This molten material freezes so rapidly that the atoms have no time to arrange themselves into crystal units, but remain in disordered array as an amorphous surface. Such a surface is known as a Beilby layer.

The first objective is, then, to produce a Beilby layer. This thin layer is harder than the corresponding crystalline form of the same material; its energy is also greater, and it therefore represents an unstable condition. In some cases moderate heating of the Beilby layer will transform it into the crystalline state, sometimes a spontaneous recrystallisation occurs. Such a transformation gives rise to cracks. It is reasonable to suppose that material alloying together of the two metal surfaces will occur more readily when they are in the amorphous condition than otherwise. This affords an explanation why it is desirable to select bearing metal of lower melting-point. In addition to the advantage of producing a Beilby layer, the crests are reduced and the dips are filled in, thereby increasing the contact areas, which in turn leads to a lower surface temperature, and less risk of alloying or pick-up of the bearing metal.

From this explanation it will now be obvious that if running-in is not properly done grave damage to the surfaces is potential. The crests can weld together, and then be torn out, leaving behind a pit, and possibly a new crest on the periphery, which in its turn will be wrenched out to enlarge the pit already formed. Finally the surface will be covered with large pits and large crests; in fact, an ideal surface for trouble. How often one meets the complaint that after the regrind of a petrol engine cylinder excessive wear has taken place, or a seizure has resulted. How necessary it is to emphasise the vital necessity of careful running-in cannot be over-stated.

In decorative painting much time is spent in preparing the surface before applying paint; so, too, in lubrication the surface must be good if the effect of the lubricant is to be satisfactory. The quality of the finish of the surface naturally is gauged by the efficiency of the machine—in other words, it is not always necessary to aim at the superlative. To expend the same amount of energy on the bearings of a garden roller as on the bearings of a racing aero engine would be ridiculous. So when we speak of good lubrication it is necessary to keep things in their proper perspective. Similarly, when adjudicating a lubricant, always assess the conditions under which it is to work.

BOUNDARY LUBRICATION

Reference has already been made to the attractive force of the surface molecules of a metal, and its ability to attract and hold fluids. It is this attractive force which produces and maintains a lubricating film, provided there is sufficient affinity between the surface and the lubricant. For this reason a material which may be a lubricant for one surface may fail on another. Clearly, the ability of a lubricant to form a stable film is dependent upon its chemical structure and physical characteristics. During recent years investigators have devoted much time and thought in an endeavour to unravel these complex problems. Clarity is coming steadily, but full daylight is not yet. Many of the old ideas are fading, but unfortunately some of them are being held from oblivion too long. The adsorption of an oil film on metal surfaces reduces friction by what has been known for years as oiliness. The term "oiliness" is intended to convey a thought on something which is difficult to define in scientific terms. It is easy to picture what is intended, and it is equally easy for the imaginative to produce a picture best suited to the individual. Oiliness has therefore drifted almost into the realm of absurdity in the endeavours to explain all the abstract problems of lubrication. To arrest this decline, the Society of Automotive Engineers has adopted the following definition:

> "Oiliness is a term signifying differences in friction greater than can be accounted for on a basis of viscosity when comparing different lubricants under identical test conditions."

Oiliness should be primarily dissociated from viscosity and purely hydrodynamic principles, and associated with extremely thin film lubrication. Hersey explains the term as referring to the mutual action of the two adsorbed layers when there is no free liquid intervening, or at least no liquid retaining its original bulk properties.

The means of studying the mechanism of boundary lubrication or oiliness is by comparison of coefficients of friction, kinetic or static. This being so, is it legitimate to ally oiliness with kinetic friction.

Experiments clearly indicate that a selective segregation of polar bodies on metal surfaces occurs which exert an influence upon the behaviour of lubricants. Exactly how this segregation takes place is not decided, but it is believed that certain "active" or polar groups in a compound are capable of anchoring that compound to a metal surface by adsorption or physical affinity, provided the compound travels within the radius of attraction of the metal molecules. The term "active" is used here to denote a physical rather than a chemical reactivity. To show the significance of segregation, Hardy measured the static friction of mineral oil containing various quantities of fatty matter. The interesting feature about these determinations is that as little as approximately one per cent of oleic acid or 0·7 per cent of castor oil in mineral oil was sufficient to lower the friction of the pure mineral oil to that of the oleic acid and castor oil, respectively. Presumably, a layer of the polar compounds is selectively adsorbed on the metal surface which carries the load.

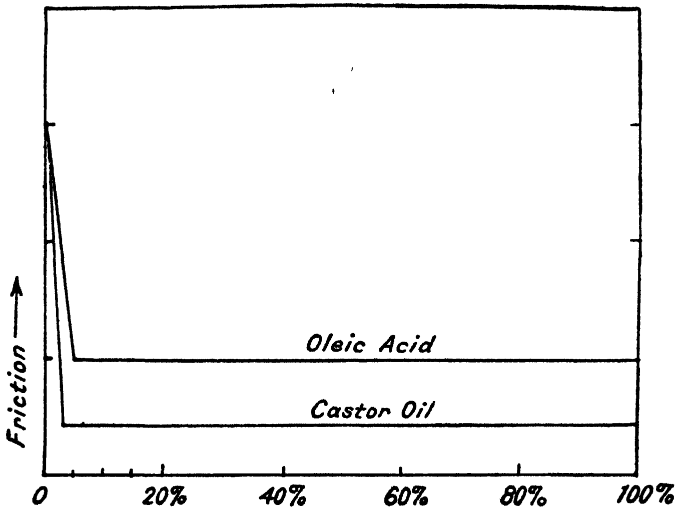


Fig. 3.

It should be mentioned that all substances which exhibit the property of attaching themselves to metal surfaces will not necessarily increase the oiliness of a lubricant.

Wilson and Barnard, in 1922, indicated that a time-lag occurs before a steady rate of flow is attained in a capillary viscometer, due to the time for orientation to occur.

Burwell and Camelford (*General Discussion*, 1937) extended this observation by tightly packing a glass tube with strands of copper wire, and passing oil through it. Rates of flow were measured at 24-hour intervals. The rate of change of flow was rapid for the first five days, subsequently diminishing, until at the expiration of about 15 days the rate remained fairly uniform. As the oil passed between the columns of copper wire, the polar constituents were attracted to the metal surface, until a continuous layer was formed. Then the rate of deposition diminished.

Fine metal powders have also the power of removing polar bodies from an oil when the two are shaken together. The ability to do so varies with different metals.

A chemically pure hydrocarbon theoretically has no polar groups, but in practice it invariably has, due to small quantities of impurities or products of oxidation. Fatty acids owe their polarity to carboxyl groups, whereas ricinoleic acid, which is obtained from castor oil, contains a hydroxyl group and a carboxyl group. Oiliness can be imparted by other groups.

The effect of chemical constitution on static friction is manifest in Hardy's results.

	Static Friction		Static Friction
Formic acid	0·45	Stearic acid	0·15
Acetic acid	0·40	Oleic acid	0·10
Propionic acid	0·31	Ricinoleic acid	0·02
Valeric acid	0·28	Lactic acid	0·20
Acetone	0·32	B.P. paraffin	0·20
Ethyl acetate	0·36	Carbon tetrachloride	0·43
Tristearin	0·24	Ethyl ether	0·33
Triolein	0·14	Butyl xylene	0·27
Benzene	0·34	Benzoic acid	0·33
Toluene	0·28	Ethyl benzoate	0·33
Xylene	0·30	Thiophenol	0·22
Phenol	0·25	Thymol	0·24
Benzyl alcohol	0·31	Castor oil	0·30

A carboxyl group does not of necessity confer oiliness, as shown by the aliphatic acids whose static friction has a range from 0·45 to 0·1. The effect of a hydroxyl group is illustrated in the lowering of the static friction of 0·31 with propionic acid, $CH_3 \cdot CH_2 \cdot COOH$, to 0·20 with α-lactic acid, $CH_3 \cdot CH(OH) \cdot COOH$, which is α-hydroxypropionic acid. The difference between oleic and ricinoleic acid is even more marked. Tristearin and triolein are the glycerides of stearic and oleic acids respectively, and form the principal constituents of fats. When the ·OH group is attached to the benzene ring as in phenol, C_6H_5OH, the reduction is from 0·34 to 0·25, similarly with thymol $C_6H_3 \cdot CH_3 \cdot CH(CH_3)_2 \cdot OH$, but when it is in a side chain, as in benzyl alcohol, $C_6H_5 \cdot CH_2 \cdot OH$, the increase is from 0·28 with toluene to 0·31.

That the effect is not due fundamentally to viscosity is shown in the table.

	Viscosity at 20° C.	Static Friction
Carbon tetrachloride . .	0·0096	0·43
Chloroform	0·0056	0·30
Acetic acid	0·0122	0·40
Benzyl alcohol . . .	0·0558	0·31

The inference is that friction can be reduced to that of the oiliness additive even when it is present in small amounts. Such a conclusion may be justified under certain conditions. It would, however, be a little unwise to have sufficient faith to rely upon very small quantities when it is necessary to rely upon the effects of oiliness addition. Very rarely does one use less than 2·5 per cent of a fatty oil in mineral oil. Suggestions have been made that 1 per cent of oleic acid will replace much larger quantities of fatty oil; in fact this suggestion has been quoted freely in the literature, perhaps a little too freely. A few laboratory experiments, useful as they may be, need extensive confirmation under carefully observed practical conditions. Laboratory experiments aim at producing as few variables as possible. Running conditions are complicated by many variables. An excellent example to prove the case is the lubrication of railway axle bearings. Here there is starting, stopping, temperature variation, acceleration, deceleration, jerking, bumping over line joints and points resulting in thick and thin oil films, sudden increased pressures when taking sharp bends, and ingress of water. Furthermore, what may be considered to be an oiliness requirement may be more in the zone of extreme pressure lubrication, where film strength is the more important. The preservation of the boundary film is the first consideration; therefore there must be an adequate supply of oiliness molecules to replace those which may be removed. Removal is bound to occur, either through rubbing force, decomposition, heat, or insufficient adhesion. Chemical resistance to decomposition is a danger which cannot be overestimated, particularly now that concentrated effort is being expended upon the production of synthetic oiliness addition agents, and the increasing loads and speeds with the attendant higher temperatures.

In the past insufficient attention has been paid to film strength in lubrication, with the result that some oiliness problems have become complicated by extreme pressure conditions. Rape oil is extensively used to provide oiliness, but it is necessary now to regard it seriously as a mild E.P. agent. Likewise, castor oil has won great popularity for gear lubrication, but it is not clear how much is due to its low coefficient of friction and how much to its film strength.

Precision has so developed in the engineer's art that protection of it has become linked with lubrication. The metallurgist is able to provide metals as wear-free as possible, but it is the lubricant which ensures the final protection. An adsorbed film should theoretically prevent wear. It would be wrong, however, to believe that an oiliness agent must essentially prevent wear, or is, indeed, the most protective material. Wear prevention must be considered separately from oiliness, and wear divided into corrosion wear and mechanical wear.

FILM LUBRICATION

Friction between two lubricated moving surfaces may be due to surface contacts or to fluid friction. The aim of the engineer is to keep the surfaces apart to eliminate surface contacts. To do this he makes provision for "thick" film lubrication. The thickness of the film is controlled by a number of factors, some of which may be beyond the control of the engineer. Assuming that complete separation of the rubbing surfaces is effected, then the only frictional factor to be considered is the viscosity of the lubricant. The advantages of film lubrication are very real, since the frictional losses are a mere fraction of those under any other régime. Continuous running of bearings at high speeds would be impossible without the intervention of a fluid film. The film of lubricant is essentially controlled by the pressure distribution within the bearing. Such a form of lubrication is a mechanical process. Owing to the difference in the diameter of the journal and the bearing, the journal is free to offset when it is revolving, leaving a wedge-shaped gap. The journal drags the adherent oil from the wide end of the wedge into the narrow end, and so builds up pressure. This results in a hydrodynamic lifting of the journal, under which only fluid friction appears. This building up of pressure within the bearing has been the subject of much study by several experimenters.

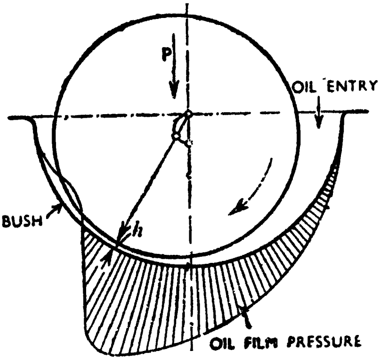


Fig. 4.—Oil Film Pressure Diagram.

The offsetting of the journal is very important, and has much to do with the thickness of the oil film at the point of nearest approach. It is at this point that the real test of a lubricant takes place. It is here that the intensive load is to be found. Consequently, anything which upsets the optimum conditions at this point will result in reduced efficiency. If the clearance is reduced to a negligible amount, the oil film will become so thin that there will be no fluid friction. Other types of lubrication, however, will be introduced which are invariably accompanied by wear of the metal surfaces. Probably the first change which will occur will be the transition from film to boundary lubrication. Excessive clearance is equally undesirable, because it will allow the passage of the lubricant through too easily, and necessitates the introduction of compensating factors. The length of the bearing is also of considerable importance. When it is long it allows deflexion of the shaft to occur, and thereby imposes an extra load on the edges of the bearing, which may be beyond the capacity of the oil film, and the strength of the bearing metal. With a very short bearing the deflexion is small and the end leakage of oil is great. The commonly accepted ratio of length of the bearing to its diameter is roughly 1·2 to 0·8.

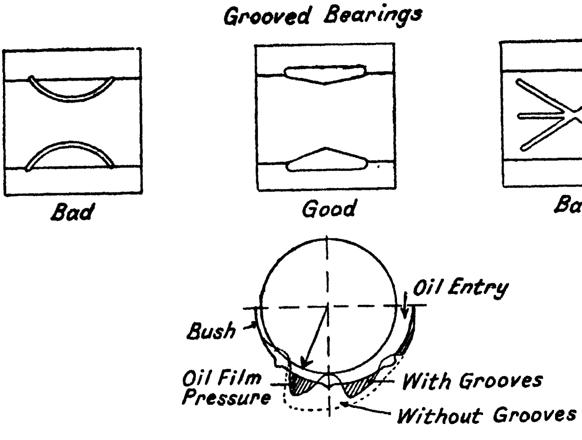


Fig. 5.—Grooved Bearings.

Many bearings have been ruined by reducing the oil film pressure through the introduction of oil grooves. It was thought at one time that grooves assisted in the distribution of oil on the bearing surface. Grooves of the right design may be perfectly satisfactory, and do perform a useful service.

For satisfactory lubrication there must be a minimum quantity of oil. Therefore, the amount fed to the bearing must be greater than the amount lost. Should it be otherwise, oil starvation would invite all the evils associated with a dry spot. In principle it matters little how the oil is fed, provided this general principle is observed. Splash feed is simple, cheap, and is suitable for moderate speeds. Ring oiling is a satisfactory system for many purposes. Preference is invariably given to force-feed oiling. It is positive, flexible, and can be applied to practically all designs of bearing, whether they be accessible or inaccessible. The oil which is fed into the bearing is invariably lost through end leakage. Obviously, the greater the clearance between the shaft and the bearing, the greater will be the chance of escape. If the ends are closed by a web on a crankshaft, or some other device, the leakage will be reduced. This checking of end leakage will automatically reduce the quantity of make-up to the bearing. In practice, this is very important, because it influences the viscosity of the oil which shall be chosen for the job.

The first consideration in lubrication is to maintain a film, and the second is to build up a definite pressure within that film. It can be done in more than one way. A viscous oil will not flow through a restricted space very rapidly. Therefore, it can build up a pressure and maintain it for a longer period than a less viscous oil, which would flow away more quickly. If the points of leakage are reduced, the flow can be reduced also, which in practice is equivalent to using a viscous oil. When the oil is fed at an increasingly high pressure to the bearing, the ultimate pressure within the film is also increased. Theoretically, by increasing the pressure sufficiently, an extremely thin oil could be used. There is plenty of evidence that we are drifting towards that goal. In motor-car practice we have seen the drift towards thinner and thinner oils. It has been made possible by better and better bearings, smaller clearances and higher oil pressures. Obviously, these are not the only factors, but they are the necessary ones to illustrate the subject under review.

When a machine is starting or stopping, a different set of conditions prevail within the bearing, and when it stops, a further set of conditions is introduced. To analyse these conditions, a clear picture of the shaft within the bearing is necessary. The diameter of the shaft is slightly less than the diameter of the bearing, to allow for expansion, distortion, and freedom to find the proper position of the shaft in the bearing when it is rotating, and to allow for the circulation of the oil. When the shaft is at rest the whole weight of the rotor is imposed upon a very small area of the bearing. That area is long, but very narrow. Sometimes it is described as "line contact." Therefore, the pressure when the rotor is stationary is comparatively great on a narrow ribbon of bearing.

When the machine is cold and stationary the viscosity of the oil is sufficient to keep the shaft off the bearings. It matters little how thin an oil film is, provided it prevents metal to metal contact. At the moment of starting the oil film is subjected to shearing stresses. The oil film may break. Even if the film does break, it may not be harmful, because the shaft will begin to climb up the bearing, leaving a greater clearance under the shaft for the oil to travel in, and when the shaft begins to fall back, it will drop on an adequate oil film. The oil which is adhering to the shaft is brought to the line of contact, and so pushes the shaft over a little to make room for more oil. The oil being fed under pressure ensures an adequate supply and stable film.

In turbine operation the risk of the film breaking is really comparatively small, because it is customary to pump oil under high pressure into the bearing before starting to lift the shaft, and to provide an oil film immediately movement occurs.

When a turbine stops after a run, a different set of conditions exist. The bearings are hot, and become hotter on standing, due to heat conveyance from the steam-heated rotor. At the high steam pressure end the bearing may reach several hundred degrees Fahrenheit. At this temperature the viscosity of the oil is exceedingly low, and the probability is that it is insufficient to prevent metal to metal contact. It is equally possible that the white metal may become plastic, and suffer thereby. It would be wrong to imagine that the whole of the white metal would become overheated. If it did it could melt and run out. Much of the heat is conveyed away through the pedestal. When the turbine is re-started there is a risk of wiping of the white metal. In fact, this does occur if precautions are not taken. Some engineers prefer to use a more viscous oil to cater for this hazard.

However good the lubricant may be, and however correctly the bearings designed and fitted, the whole thing can be a ghastly failure if the lubricant is fed into the bearing at the wrong spot. The film pressure distribution diagram makes it clear that nothing must be allowed to interfere with the building up of oil pressure as it approaches the point of nearest approach. Oil grooves, if incorrectly made, will reduce the oil pressure. Should the oil feed be very near to the point of nearest approach, there will be insufficient opportunity for the requisite oil pressure to build up. If the oil feed is at the point of nearest approach, it is practically certain that disaster will ensue with surprising rapidity.

The viscosity of an oil within a bearing is not constant. First, there is a reduction due to frictional heat, and then an increase due to pressure. Bearing pressures encountered in practice are not usually sufficiently high to make much material gain in viscosity, but in certain cases the built up pressure within the oil wedge may attain considerable dimensions. Loss of viscosity with increase of temperature is something of the order of 2 per cent per degree Fahrenheit. Oils of low viscosity appear to change little with temperature, merely because the units are small, whereas a thick oil appears to change a lot, owing to the larger numerical values. A good deal of confusion has occurred through this one fact. Temperature-viscosity characteristics vary considerably with oils of different origins and methods of refining. More will be written on the subject under the heading of viscosity index. Similarly, the effect of pressure on viscosity varies with different oils. Mineral oils have a comparatively high sensitivity to pressure, whereas fatty oils are much less affected. Oils of high viscosity lead to high friction; consequently, fatty oils, when operating at very high pressure, must give lower friction than mineral oils. Some experimentalists in the U.S.A. have used this fact to suggest that oiliness may be nothing more mysterious and complex than pressure-viscosity effects.

CHAPTER VI

DEPOSITS

An engine running under ideal conditions takes in nothing but fuel, lubricating oil and air. Whilst reasonable care is taken to exclude foreign matter from the fuel and lubricating oil, insufficient protection against the ingress of dust in the air is provided. Obviously, the amount of dust in the atmosphere must vary enormously with the locality. The modern surfacing of roads has done much to eliminate road dust, but road dust still remains in the air, which is drawn into the engines on the road. In some cities as much as four tons per square mile per day of dust falls. In a reasonably clean atmosphere an engine may breathe 46 grams of dust per year into the combustion spaces, and upward of 2 grams into the crankcase through the ventilating system. To deal with this enemy, air filters are fitted. Most motor vehicle manufacturers realise the need for air filters; they are saddled, however, with the responsibility of deciding whether to employ a large efficient filter or a small one of less efficiency. Space and cost are usually the deciding factors. When operation is conducted in exceptionally dusty atmospheres, such as Libya, very special precautions must be taken if the life of the engine is not to be measured in hours.

Road dust invariably contains a large amount of silica as sand or in combination with lime, magnesia, etc. In either form it is abrasive, and can grind away a measurable quantity of iron in a finely divided state. The road dust may remain in the combustion space in admixture with the oil and finely divided iron. Iron, particularly when finely divided and at a high temperature, is an active oxidation accelerator for the lubricating oil, which is revealed as solid oxidation products in the combustion space. Most people call these solid products "carbon," in the firm belief that they are wholly or mainly carbon. Unfortunately they are quite wrong. So-called "carbon" is a complex mixture of oxygenated compounds. Even the portion which is insoluble in benzene contains a considerable quantity of combined oxygen. Doubtless its insolubility is due to its more highly oxidised character, and not to its approach to pure carbon.

The dust which passes the rings into the oil sump is partly arrested by the oil filter in the by-pass system, part by the wire gauze, and part by sedimentation. That which is lost by sedimentation is of too large a particle size to circulate, and is therefore harmless. The large particles are collected on the gauze, and choke it. Small particles flow round the engine suspended in the oil, to cause damage when they are temporarily gripped between two metallic surfaces. If they are not gripped, but pass on in the oil stream, no abrasion can occur. Again, finely divided iron is formed to start and accelerate oxidation in the crankcase with the formation of solid oxidation products, which may deposit around the piston rings, or under-side of the piston, or remain as sludge in the oil. The composition of these products is very similar, if not identical, to that on the piston crown.

How far fuel will give rise to deposits is uncertain through bad combustion. It is often assumed that soot does form, particularly in diesel engines. Direct evidence is not very strong. Turbulence in the engine is conceivably high enough to ensure that the microscopic particles of soot are expelled through the exhaust valve. There are, however, sometimes undesirable constituents in the petrol in small amounts which are known as gum. Just what they lead to is uncertain, but it is reasonable to suppose that they form deposits. This is a very controversial subject.

Since that marvellous discovery, by Midgley, that tetraethyl lead would admit the use of higher compressions, another potential source of deposit has been introduced. Every known precaution has been taken to suppress the deposition of lead oxide from the petrol containing this knock inhibitor. However, when it is realised that if 700 gallons of petrol are consumed in an engine in one year, 580 grams of tetraethyl lead, or nearly 400 grams of lead, pass through the engine, there is an added source of deposit. Such a possibility is not so easily understood when we think of the 0·5 ml. of tetraethyl lead contained in one gallon of petrol. When examining a deposit, it is prudent to look for lead, particularly in aero engines. Purely as a matter of interest, it is alleged that during the teething troubles of tetraethyl lead some of the lead bromide led to the formation of magnetic oxide of iron. Some of this pyrophoric iron was shot out of the exhaust on to the wing of an aeroplane, and produced a fire. This incident is mentioned to illustrate one of the many problems which face the producer of new developments.

It might rightly be alleged that these contributory causes of engine deposits are eclipsed by the formation of deposits from the lubricating oil. Any auxillary forces which might be operative cannot be neglected when examining a deposit from an engine. Cases are on record where over 90 per cent. of the total deposit were either oxides of lead or iron.

Mysterious seizures of engines have been traced to deposits which offered little resistance to the engine when hot, but when cold have set solid. In these cases, glycerol had been used as an anti-freeze, and had leaked into the engine, where it decomposed. There was not much difficulty in establishing the cause in these cases, as free glycerol was found in the oil. Leakage of cooling water has often given rise to the deposition of water soluble salts on the piston crown. In one case, a most unusual deposit was found, and the author traced it to the fact that molasses had inadvertently been put into the engine by a farm labourer. Another similar instance occurred in Egypt, when a native drained oil out of a sealed tin through an unsoldered joint and refilled with honey.

Sometimes in the ash of a deposit is found measurable quantities of an assortment of metals. By a little careful thought it is usually possible to make an accurate estimate of their origin. Copper, as might be expected, is very common. It might have come from piping, copper alloy bearings, bronze bushes or gears. Brass can give rise to copper and zinc, but if zinc is present, galvanised tanks or pipes must be suspected. Just what significance zinc has in a deposit has not been explained, but whenever it occurs, it must be eliminated from the system to cure the trouble. Years ago galvanised iron oil tanks were used in turbines, until it was realised that they were a continual source of anxiety. The presence of tin may indicate that white metal bearings are being wiped or failing. Calcium and magnesium may simply be constituents of road dust, but it is prudent to look further, because they may indicate leaking cooling water, or priming of a boiler. Sabotage is so unusual that it is hardly worth mentioning; however, it may happen, therefore unusual things may be found. It is not within the scope of this book to suggest what could be used. Carborundum could be used by the saboteur; in fact, it has been tried, but not very successfully, because it separates in the oil sump. Before coming to a rash conclusion, remember that carborundum is used for honing and in grinding pastes.

From the examination of a vast number of deposits from petrol engines run on the road, and on the bench, it is difficult to reach many useful conclusions. All efforts to standardise the methods of examination of deposits and used oils have failed, due to the lack of support for the proposed procedures. Consequently, whatever system is adopted, it is certain to be criticised. The chemist who is not a specialist in oils is therefore well advised to follow any course which will tell him whether a deposit is normal or an abnormal one. For routine purposes the author is content to extract the free oil with petroleum spirit (B.P. under 40° C.) in a Soxhlet, and follow on with a benzene extraction. The ash is determined in the orthodox manner. By this method something at least is revealed. Should the oil content be high it is reasonable to suppose that an excess of oil has been passing the rings. Several things are indicated such as unsuitable oil, stuck rings, worn rings, worn cylinder, or badly fitting rings. A soft deposit is frequently due to a high oil content. High ash always calls for a detailed analysis to ascertain whether it is due to road dust, graphite, metal particles or corrosion. Should the benzene insoluble be unusually excessive it may be traced to carbon from incomplete combustion of the fuel. When this occurs it is useful to make an analysis of the exhaust gas, and to suggest attention to the air/fuel ratio. Should an exhaust gas analysis be attempted care must be taken to obtain the sample sufficiently high up in the exhaust pipe to eliminate air contamination.

EXHAUST GAS ANALYSIS ON 14 H.P. CAR

Speed	Air/Petrol	CO_2	O_2	CO
		Per cent	Per cent	Per cent
Tickover .	9·5 : 1	5·4	1·6	13·2
25 m.p.h. .	10·5 : 1	9·0	nil	7·8
40 m.p.h. .	13 : 1	12·0	nil	2·6

The presence of oxygen when the engine was ticking over is due to air contamination.

By this system of examination fairly wide tolerance must be allowed even for a normal deposit for a variety of reasons. Allowances must be made for the general condition of the mechanical parts, interval between decarbonisation, treatment of the engine and composition of oil used. A few results will suffice to indicate what to expect from combustion space deposits.

It was thought, and still is thought by some people, that the benzene insoluble is carbon. The sooner this belief can be eradicated

Oil	Benzene Soluble	Benzene Insol.	Ash	Silica	Copper	Iron	Calcium
5·8	5·9	73·2	15·0	7·1	3·6	80·2	8·9
6·5	1·7	65·8	15·0	6·9	5·5	82·2	5·5
12·0	4·1	76·3	7·6	nil	7·7	88·8	2·9
5·9	4·5	43·5	46·1	nil	16·5	72·0	11·0
6·1	1·7	88·2	4·0	19·3	3·2	74·1	2·6

the better, because it has led to misunderstandings and incorrect conclusions. Both the benzene soluble and insoluble are mainly oxidised oil. Many ultimate analyses have shown this to be true. Ultimate analyses have also shown that the benzene insoluble matter contains more combined oxygen than the benzene soluble. Analyses of deposits taken from three widely different cylinders illustrate the accuracy of this statement.

		Benzene Soluble Per cent	Benzene Insoluble Per cent
Diesel Engine :	Carbon	70·3	60·1
	Hydrogen	8·8	4·7
	Oxygen	20·9	35·2
Steam Engine:	Carbon	85·2	77·0
	Hydrogen	10·8	5·9
	Oxygen	4·0	17·1
Air Compressor:	Carbon	78·2	72·1
	Hydrogen	9·0	5·9
	Oxygen	12·8	22·0

The insolubility may be due to the more highly oxidised character or to the formation of organo-metallic compounds.

Under the furnace conditions in the combustion space a host of things might be anticipated. An analysis of the temperature gradients on the various metal faces will remove some of the hasty conclusions. Cylinder walls are designed to be cooled either by liquid or by air to prevent distortion and destruction of the metal by heat. Piston crowns are attached to skirts for mechanical guidance, and to convey the heat away. The fact that aluminium can be used for their construction is sufficient proof that they do not reach the melting-point of this metal. The temperature to which the thin oil film is exposed on the crown is between 300° and 650° F. This is confirmed by the fact that piston crown deposits invariably contain free oil. An interesting fact is that at moderate operating temperatures the weight of deposit is usually greater than at higher temperatures, the explanation being that the carbonaceous matter is burnt off. To keep an engine clean it is considered good practice to vary the speed or load within the safety limits. A speeding up of the engine also increases the oil flow, and so flushes the working parts and oil pipes to remove loose deposits. A point which has been frequently noticed with petrol engines on the bench is that although the total amount of deposit after one day of running may be almost as much as after three or four days, it is softer and more oily. During the prolonged exposure to the high temperature of the gases the oil is evaporated or burnt and the deposit becomes harder. It is also possible that increased oxidation may occur, but this will depend upon the amount of free oxygen available. Only scanty evidence is available that the deposit turns to residual carbon in the burning away.

DIESEL DEPOSIT USING RICH FUEL MIXTURE

Benzene Soluble	Benzene Insol.	Ash	Silica	Copper	Iron	Calcium
5·1	93·1	1·8	6·9	5·7	84·6	1·5

Reference is sometimes made to hot sludge and cold sludge in the crankcase of petrol engines, the justification being that cold sludge is more common in cold climates. As the term "sludge" is so descriptive and all-embracing, serious objection cannot be taken against the two descriptions, although they are unfortunate. When petrol burns it gives rise to carbon dioxide and water. Very roughly, a gallon of petrol creates a gallon of water. Under normal running the steam is exhausted from the combustion space in the normal way. At the moment of starting there is excessive ring clearance, consequently a little steam can be blown past the rings into the cold crankcase where condensation can occur. If the engine warms up reasonably quickly it is vaporised and expelled through the breather. When the temperature is below freezing-point it may solidify in minute particles, and be carried round with the oil to be liquefied and emulsified. Centrifugal force then deposits the emulsion on still parts. When this cycle does not exist emulsions can still form through the condensation of air moisture in the crankcase when the air is compressed, provided the temperature is sufficiently low. Any set of conditions which enables water vapour to condense and contaminate the oil may lead to emulsion deposits. With used oil the readiness to emulsify is greater than with clean oil, because it contains emulsifying materials. The ordinary sludge is hot sludge, and cold sludge is ordinary sludge mixed with emulsion.

COLD SLUDGE

Water	Oil	Benzene Soluble	Benzene Insol.	Ash
35·0	51·6	2·9	8·7	1·8
11·0	67·2	3·5	12·9	5·4

It is not necessary for the sludge to separate on the still parts of the engine. It is still sludge even if it is in the oil as a suspension.

Crankcase sludge is also an oxidation product of the oil. The oxygen content is very similar to that in the combustion space deposit. In this category it is convenient to refer to sludges found in oils other than petrol engines.

	Water	Oil	Benzene Soluble	Benzene Insoluble	Ash
Turbine .	64·6	35·2	0·11	0·07	0·07
Turbine .	69·6	19·1	5·3	4·5	1·5

The ratio of benzene soluble to benzene insoluble in the petrol engines, and of course aero engines, is somewhat less than in the combustion space deposits. Probably this is attributable to the shorter space of time which the sludge has been exposed to high temperatures. It must not be forgotten that when the oil is circulating it may remain for considerable times in the piston ring area before it is washed away, and can therefore reach a high temperature. So some similarity would be expected. The presence of tin is indicative of bearing metal. In the two samples which contain lead, suspicion would be centred upon tetraethyl lead. Actually leaded fuel was used in each engine.

In gears and turbines it is unusual to encounter very high temperatures, consequently it is not surprising that the benzene soluble is sometimes considerable less than the benzene insoluble. Where the reverse is the case it will be noted that the ash is very high. The

Oil used	Oil	Benzene Soluble	Benzene Insoluble	Ash	Silica	Copper	Iron	Calcium	
Petrol	76·2	6·3	15·0	1·3	12·8	—	73·9	—	8·3 tin
,,	59·4	4·7	24·0	11·9	13·2	—	18·4	—	6·2 tin 58·6 lead
Aero	58·0	4·8	23·3	13·9	—	2·7	17·5	—	79·0 lead
Gear	37·8	23·7	11·2	27·3	13·2	—	85·0	—	—
Turbine	25·3	69·6	4·4	0·7	10·3	32·3	28·7	2·0	23·6 zinc
,,	—	—	—	98·7	14·0	1·4	84·0	—	—
,,	13·6	0·8	42·6	43·0	4·6	10·2	66·6	13·3	2·6 zinc
,,	26·3	1·7	20·0	52·0	29·2	—	68·8	—	—
,,	—	79·3	0·7	20·0	1·6	39·9	57·6	—	—
Gas Compressor	21·1	13·9	63·9	1·8	9·1	—	59·6	17·8	11·6 lead
Steam Cylinder	14·1	3·6	77·2	5·1	11·3	4·7	83·2	—	—
,,	13·8	3·2	58·3	24·7	60·4	—	31·4	5·8	—
,,	6·1	1·0	86·4	6·5	4·2	—	59·6	6·9	—
,,	40·6	5·1	7·7	46·6	—	—	—	—	—
,,	16·4	2·6	80·1	0·9	—	—	—	—	—
Transformer	40·8	17·3	35·5	6·4	—	96·0	2·7	—	—

turbine in which the sludge was wholly ash was new and still contained moulding sand.

The sludge in the gas compressor oil is included because the benzene soluble contained a large proportion of naphthalene.

Steam cylinder oil solids are characterised by high benzene insoluble similar to combustion space carbon, except that the oxygen content is a good deal less. One exception is given. The probable explanation is that the high oil content indicates little exposure, and the high ash accidental contamination. On inquiring, it was acknowledged that a shut-down had been ordered due to serious priming of the boiler.

Sludges in turbines are often composed of viscous emulsions. There is no regularity about them. When they are examined the difficult task of tracing the emulsifying agent should be attempted. All sorts of adventitious materials are possible, even wet paint!

Prior to starting an examination of a deposit, as much information as possible should be obtained about the running conditions and the reasons why the examination is requested. Sometimes details are difficult to obtain, but this should in no way deter the chemist from pressing for them. They will save him a lot of time and difficulty, and will assuredly enable him to write a much more intelligent report. Deposits are usually too complex for an ordinary chemical analysis, so powers of observation and deduction are called for. Should the sample be sticky or gel-like a fatty oil is suspected, and can be confirmed by the saponification value of the extracted oil, or if further evidence is required by separation of the fatty acids and their constants determined. Emulsions vary in colour according to the contaminants, but they invariably possess a blanc-mange-like structure, sometimes soft, sometimes stiff. Smell often indicates the type of machine used. When a report is prepared it may fall into the hands of one who will ask what the individual figures mean. The reply might well be that the data are accumulated to ascertain whether the deposit is normal or abnormal, and whether any deductions can be drawn. If the work is viewed in this light it will lighten the task.

DEPOSIT FROM PISTON HEAD OF PETROL ENGINE

Solvents taken in following order:

Alcohol — 11·4 per cent soluble		C	81·98
	F.F.A. ≡ 25·6 per cent as oleic	H	11·48
	Sap. Val. = 53·1 mg KOH	O	6·54
	Acid Val. = 51·1 mg KOH	Ash	nil

P.E.$>$40° C.	— 6·78 per cent	C	86·07
		H	12·41
		O	1·52
		Ash	nil
C_6H_6	— 2·70 per cent	C	83·39
		H	10·57
		O	4·04
		Ash	nil
Pyridine	— 5·8 per cent	C	72·13
		H	5·26
		O	19·89
		Ash	2·72

DEPOSIT FROM PISTON HEAD OF AIR COMPRESSOR

Solvents taken in following order:

			Ash free
P.E.$>$40 —15·4 per cent soluble	C	83·53	85·06
	H	10·48	10·68
	O	4·20	4·26
	Ash	1·79	
C_6H_6 soluble. — 10·2 per cent	C	72·93	78·85
	H	7·90	8·54
	O	11·60	12·61
	Ash	7·51	
C_6H_6 insoluble	C	43·50	84·03
	H	3·65	7·04
	O	4·64	8·93
	Ash	48·21	
CCl_4 sol.—2·74 per cent	C	65·65	69·66
C_5H_5N sol. 18·10 per cent	H	5·01	5·32
	O	23·59	25·02
	Ash	5·75	
Insol. Residue	C	45·48	74·43
	H	2·99	4·89
	O	12·64	20·68
	Ash	38·89	

CHAPTER VII

SELECTION OF LUBRICANTS

ALL the devotion which has been given during recent years to chemical, physical and mechanical tests has aimed at providing assistance to improve lubricants, and to find means by which a better selection of lubricants can be obtained. Tests in their various forms do provide information which can often be applied very accurately. There is plenty of evidence to support this contention as will be seen as this subject develops. Some tests are less positive, but they point the way to a conclusion. Because lubrication is surrounded with variables it must follow that tests must be devised which will embrace all of them, or a series of tests introduced which can be considered collectively. The importance of "Standard Tests" lies in the fact that all results are comparable and, so far as possible, accurate, and that everybody has access to the same set of tools to fashion a conclusion. Criticism is often levelled against laboratory tests, and a call made for observations under actual operating conditions. Before conceding to the call it is well to ask whether the owner of an expensive and powerful machine would hazard the risk of its destruction merely to satisfy a lubrication difficulty. Further, would the cost of running such a machine for experiment justify the result? Often the time taken to achieve a result would be too great. Obviously small scale inexpensive routes must be chosen to investigate the probable behaviour before proceeding to the final arbiter—the engine.

There is scarcely a piece of mechanism which is not beset with lubrication complications. The pleasures derived from the average lawn mower can be converted into hard labour by a disregard of correct lubrication. To many gardeners "just oil" is required periodically. The difference between the effects of a suitable oil and unsuitable lubricant is surprising—often it is just that difference between pleasure and displeasure. An oil which produces gum introduces unnecessary friction; likewise an oil of unnecessarily high viscosity can be readily detected by the extra energy required. There is a great temptation to put grease or viscous oil on the spindle of the driving roller, because of the difficulty of lubricating it when assembled, in the belief that it will remain effective for many weeks. If one should yield to the temptation, much sweat will be the reward. It is better to spend a few seconds with the oil can regularly. The makers of Yale locks practically forbid the use of oils simply because they cannot afford to risk the formation of gum in the locks. Many makers of sewing machines sell lubricating oil for no other purpose than to ensure the proper lubrication of the machines.

If common household mechanisms need special care how much more is required for the many moving parts which have become part of our civilisation. Probably the motor-car has done much more than anything else to make the people of the world oil-minded. The motoring public is almost fanatical about its engine lubricants, and as long as it has a regard for its engines long may it remain so.

Big fleet owners can be superficially less critical, but in fact they are more critical. By the employment of skilled engineers and chemists they can make expert examinations and repairs, and thereby keep a constant eye upon the behaviour of the oil. They can, in fact, if they so wish, afford to take a risk which might be ruinous to the owner-driver or contractor not so well protected. By this there is no implied suggestion that the little man chooses good oil and the big man less good oil. It simply means that if the big man decides upon a lower quality his hazards may not be so great or devastating to the purse. Many of the big transport undertakings have decided by experience to use very high quality oils. The War Office, through the sound judgment of its highly trained officers and advisers, has specified lubricants of the highest quality for all its mechanised equipment. The Royal Air Force is equally well supplied. Owners of large steam turbines are ever ready to take advantage of any improvement in turbine oils, and keep a constant vigil over it during its life. It is possible to go over a long list of engineering interests and show that in the main there is a preference for the higher grades of lubricants. Therefore if there is a doubt about the selection of an oil, it is prudent to err on the extravagant side and not in parsimony.

If it is good practice to use good oil, then it is economical to provide it with good conditions. This seems almost like stating a postulate. The arm-chair scientist will probably hold that it is, but those who bump up against realities know how frequently lubrication is left to shoulder its own responsibilities. When an engine is new it contains sand in the castings, dust on its components, and metal particles on the machined faces, all of which are removed by oil flushing into the sump, and recirculated in the oil flow, ever ready to damage good fitting parts, or collect in a dangerous area. To guard against such damage petrol engine builders insist upon the engine being drained after the first 500 miles. Where it is not possible to remove the first fill of oil much relief can be obtained by some system of efficient filtration, or if this cannot be done, by removal of the foreign matter by sedimentation. Should it be possible to clean a mechanism either before or after assembly it should be done. During operational conditions devices should be designed to keep foreign matter out of the lubricant, and at convenient intervals filtration ought to be applied. In dusty atmospheres special precautions are necessary. During the war in Libya air filters of generous dimensions were a necessity to the mechanised armies. It has been stated that an internal combustion engine could be ruined in that country in a single day if it ran without an air filter.

Engines with an oil circulating system accumulate, in addition to external dirt, products of oil decomposition, acids, fuel or condensed steam. Whatever measures are taken to remove them, a time comes when the whole of the oil must be withdrawn, and a charge of new oil put in. The practice of flushing is gaining in popularity. When a turbine is emptied it is often filled with a second grade turbine oil and run for a few weeks before the refill with the first grade oil is made. The flushing oil after filtration can be used again. Turbine oil coolers accumulate a quantity of sludge. In the past it was regarded as a necessary evil, and too big a job to remove it. Now that has changed. Systems have been invented to remove the sludge from the cooler in situ by vaporising solvents. Solvents are also used to dissolve the sludge from many engines after draining. A motor-car engine can be cleaned in about fifteen minutes without dismantling any part of it except the bottom drain plug. The old idea of flushing the engine with a cheap thin oil or kerosine simply dislodged the solid by oil flow, and left behind that which was not subject to sufficient oil bombardment. Solvents are complete in their action, because they actually dissolve the sludge as well as bombard it. Tetrahydro-naphthalene has been patented for this purpose.

Treating surfaces with paint, gold size, and lacquers have been sources of trouble through their interaction with oil. Even galvanising of oil tanks is to be discouraged. Free generated acid in the oil attacks the zinc, giving rise to zinc soaps.

The first consideration in the selection of a lubricant is whether it shall be mineral, fatty or both. An exclusive use of fatty oils is so exceptional that they require very little attention. Castor oil was used in rotary aero engines principally to overcome dilution with petrol. The solubility of castor oil in petrol is limited whereas mineral oil is miscible. Therefore, if it is desirable to use a lubricant in conjunction with a solvent it may be necessary to choose one which is insoluble. Should the solvent be alcohol, then one would avoid castor. Castor is the only common fatty oil which is soluble in alcohol and insoluble in petroleum. In common with petroleum it is soluble in benzene and aromatic hydrocarbons. The disadvantage of castor oil is its tendency to gum and form rubber-like compounds at elevated temperatures, particularly in the presence of finely divided iron and copper. Lard oil is still claimed by some to be par excellence for metal cutting. In the old books considerable support was given to it. Since then views have changed somewhat. Other cutting oils have been introduced. Lard oil has not indefinite keeping qualities—it goes rancid. Also, in cold weather it freezes. To attempt to start work in a cold shop with a solid oil is a nuisance. Rape oil has superseded lard extensively for cutting, largely because it has a much lower pour point and is freer from odour. Solid tallow has found application for the lubrication of hot necks on rolling mills, where it melts and flows slowly on to the bearing. Neatsfoot and porpoise oils, after separation of higher melting-point constituents, are used for watches, clocks and fine instruments.

As a temporary expedient for heated bearings castor oil has long been known. A few drops will often effect a dramatic cure. The explanation is simple. Castor oil has a very low coefficient of friction, so it re-establishes a film and reduces the friction. The heating is often caused by a partial, or perhaps total, rupture of the oil film. Sometimes a little flowers of sulphur is used for the same purpose. Primarily it acts as a solid lubricant, then it melts and sulphurises the remaining oil, and so acts as a mild extreme pressure lubricant.

Compounded oils of fatty and mineral oils may be regarded as substitutes for fatty oils. Actually the fatty oil orients itself on the metal surfaces and the mineral oil is sandwiched between the layers. How much selective adsorption occurs clearly depends upon the proportion of the fatty oil present. More about this subject is given elsewhere. The coefficient of friction of fatty oils is generally lower than that of mineral oils, or to use a popular expression, they possess greater oiliness. Then, compound oils are used for conditions which need greater oiliness than can be provided by mineral oils. Locomotive axles are often lubricated with oils containing rape oil, not because they are necessarily heavily loaded, but because they are shock loaded. As they pass over line joints, points and unevennesses of track, violent upward thrusts occur. An engine pulling a train at sixty miles per hour and above often causes the bogie wheels to wander and the driving-wheels to lift off the rails more than one inch. Such violent shocks on the bearings necessitate carefully considered lubrication to avoid hot boxes. Marine reciprocating engine bearings are usually lubricated with oils containing blown rape or fish oils. The reason is that if the bearings run hot the oil film is not destroyed if sprayed with water. The blown oil acts as an emulsifying agent. Water in a bearing using mineral oil can gradually dispel the oil; consequently, if water can contaminate the oil film it is advisable to consider the use of a compound oil. Sometimes air compressors working in very humid atmospheres are lubricated with compound oils as the water vapour liquefies on compression. Fatty oils often increase combustion space deposits in internal combustion engines, but they can also offer some relief to deposit formation. Gas and oil engines are frequently lubricated with compound oils. For metal cutting, lard oil used to be used, but now it is generally blended with mineral oil. Heavily loaded bearings can be lubricated with viscous oils to provide a thick film, but if it is not advisable to use a thick oil extra film strength can be provided by the introduction of rape oil. Another use for fatty oils is to increase the viscosity index of mineral oils. Whenever boundary lubrication has to be considered it is well to remember that fatty oils will give a safer film than mineral oil. Conditions may exist which preclude the adoption of a compounded oil, such as gumming or acid formation.

If in doubt it is safer to select a mineral oil. A compound oil should not be chosen unless reasons for its use are given or are understood. This warning is not given to create fear, but rather to indicate a safe course to those whose knowledge of lubrication is limited. Mineral oils are almost universally used for film lubrication, excluding the cases already given.

Appearances of oil, except to the specialist, are most deceiving. It is impossible to judge the quality by sight alone. Colour does, of course, mean something, but it is too complicated to discuss in detail. The average user need not pay too much attention to it beyond such obvious differences between white, yellow, red and black when viewed by transmitted light. By reflected light the fluorescent tints will be observed.

The most important physical characteristic is viscosity. There is no simple method for ascertaining the optimum viscosity to use for any specific mechanism. The specialist just knows from experience and general practice. Selection of viscosity limits is controlled by a number of factors, e.g. temperature, load, method of feed, speed, etc. Generally low viscosity oils are used for light loads and high speeds, and higher viscosity oils for heavier loads and lower speeds. Such a generalisation is not of very much practical value. A closer consideration will be given in the chapter describing oils employed. Temperature looms high in the list of considerations. In arctic climates a medium viscosity oil is used, because at that temperature it is very viscous. Bearings operating at high temperatures may require a bright stock, or other steam cylinder oil. Then there is the machine which is used over very wide temperature ranges. When this occurs it is impossible to select an oil which has the correct viscosity over the whole temperature range, consequently a compromise is necessary. What that compromise is depends upon the conditions. Should the maximum temperature only be reached for short periods at rare intervals some risk can possibly be taken by adopting a low viscosity at that temperature, but if the main operating temperature is high then more attention must be paid to viscosity. Starting at low temperatures is always a source of anxiety. So much depends upon the complexity of the machine and the available power to overcome viscous resistance. There is invariably a maximum viscosity for starting temperatures. A simple case to illustrate the point is the petrol engine in a transport vehicle. It may be required to start under arctic conditions and then run hot in mountainous country. An oil with a viscosity of over 10,000 seconds (Redwood) would make starting very difficult, therefore the first thought is to select an oil not above this viscosity at the starting temperature, which may be 0° F. or −40° F. To ensure a reasonable viscosity at running temperature a high viscosity index oil would be chosen to provide as high a viscosity as possible. Sometimes the optimum viscosity for a job is completely overruled by the capacity of the housing to retain oil. Most gear boxes are difficult to make tight so an unnecessarily thick lubricant is used. Thick lubricants are often used to damp noises, or to assist a bad fit, or to reduce consumption.

Specific gravity used to be quoted in nearly all specifications, but in recent years the practice has diminished. To differentiate between different types of oils it is useful if considered with other data. The Penna type has a lower gravity than the Texas type, and the more paraffinic type has a lower gravity than the naphthenic or asphaltic type. To guess the origin from the gravity would lead to difficulties, because types are not wholly peculiar to localities. Since the introduction of solvent refining low gravity oils can be produced from many crudes, irrespective of the locality in which they are found. Admittedly if three oils of equal viscosity are found to have different gravities it may be expected that the one with the lowest gravity will be Penna, the intermediate Mid-Continent, and the highest Californian or Texas. This expectation might, of course, be entirely false in the absence of other data.

For some purposes it matters little what the gravity is, or for what its association stands. There are many applications for which certain characteristics, which are only associated with low gravity, are essential. The mere quotation of these automatically demands a low gravity. How long this will persist nobody can predict, because already additives have been discovered which, when added to oils, will increase their viscosity index. The distinction between high and low gravity oils is gradually being narrowed. But still the affection for low gravity oils is strong. Faith in an old picture is difficult to dispel. Whatever the affections may be for the idea that low gravity oils are the more stable, care should be exercised during the transition period through which we are passing, due to research and advancement. Stability is a function of the conditions of service.

It has long been a practice in the trade to sell lubricating oil at the rate of 9 lb. to the gallon. Hence, with high gravity oils less than a measured gallon will be obtained, and with low gravity oils more than a measured gallon. Criticism has been levelled at this practice especially by those who purchase by weight and sell by volume. The practice was adopted because the oil is invariably filled into containers at a temperature above atmospheric to reduce the viscosity and so speed up output. Furthermore, the oil should be passed through 60–100 mesh wire gauze immediately prior to entering the container, consequently it must be heated for it to pass through in a reasonable time. The practice is now being superseded by volume measurement especially where small packages are used.

Viscosity index is a very convenient way of conveying a mental picture of change of viscosity with temperature; the higher the numerical value the less the variation. Ideally, it is usually an advantage to use a high V.I. oil to ensure as narrow a viscosity range as possible, particularly when the temperature range is substantial. Practically, however, it is not always possible. Refrigerator oils must possess a very low pour point. Such oils are associated with the higher gravity and low V.I. categories. Price and economy often determine whether a high V.I. oil shall be used. Viscosity index is comparatively new, although the practice of quoting ratios or maximum and minimum viscosities at different temperatures is old. A little care is desirable in becoming infatuated with a new thing until its significance is reasonably well understood. In other words it would be imprudent to make a dash at high viscosity index for all and sundry purposes, and believing when faced with a selection that the highest V.I. is necessarily the best. For petrol engines it would probably be a safe choice, but for many diesel engines it would be better to choose a medium V.I. oil.

Flash point was primarily devised to ascertain the liability of an oil to emit sufficient vapour to form a fire hazard. Fire insurance companies are naturally interested in the flash point of oil stocked by their clients, and in order to meet the demands of the insurance companies oil users are interested in flash point. Fortunately, policy holders are not worried so much with actual flash point, but with scheduled ranges. The common carrier, such as railway companies, has also some concern to safeguard all the commodies it carries. Beyond these and similar requirements flash point has very little interest to the user. It has no relationship to lubrication values, consequently it is common practice to demand or quote a minimum flash point to ensure safety. This figure often looks absurdly low, but let it be remembered that it may be many degrees below the actual value. A petrol engine oil invariably has a flash point well above 400°F., but after a short period of service in an engine it drops considerably due to contamination with petrol. Flash point is useful for detecting contamination with low flash materials, and blends made with a low flash constituent. In the case of straight run distillates the flash point rises with increase of viscosity, but with blends correlation is too erratic for such a conclusion. Care must be exercised in preventing confusion between the ignition of oil by a flame and the ignition by a hot body. The two are quite distinct, and the hazards well apart.

Spontaneous ignition temperature is the temperature at which ignition can occur by a hot body. If a bearing heats up the oil can be fired. A year or two ago a phosphor bronze bearing heated up, disintegrated, and a portion fell into the crankcase of a large diesel. Immediately a violent explosion took place. Evidently the concentration of oil-vapour or atomised oil was within the explosion limits. Fires have been started by oil dropping on to steam-pipes. Axle boxes have issued flames through overheating. Careless storing of oily rags has permitted sufficient heat to be generated to start spontaneous ignition.

Loss on evaporation is so dependent upon the method by which it is determined that it is only considered on rare occasions. Many efforts have been made to excite interest in it without much avail. Practically, it is difficult to distinguish between vaporisation and atomisation. Both must take place simultaneously in a working mechanism, and both contribute to the oil fog which is visible. High speed spindles in textile mills cannot resist atomisation as they fling the oil off with considerable centrifugal force. Bombardment of rapidly revolving gears with a jet of oil creates violent splashing and disintegration, and in so doing exposes exceedingly large surface areas of oil from which vapour can arise. The static surface in an oil cooled electric transformer, maintained at any temperature up to 90° C., offers an ideal condition for evaporation loss, consequently it is customary to determine the loss on evaporation of a transformer oil.

Breakdown value (B.D.V.)or dielectric strength is of importance to transformer and switch oils. It indicates the insulating value, by proving the absence of moisture and fibre which, if present, would bridge the gap and allow an electrical discharge to pass. B.D.V. is also useful for detecting small quantities of moisture in SO_2 refrigerator oils. Traces of water either in the oil or in the sulphur dioxide are originators of trouble. This test for suspended water droplets is very sensitive.

Pour point is an essential to everybody who is concerned with low temperature starting or operation. Although attention is being given to viscosity at low temperatures it is prudent to know the pour point. It indicates the temperature zone where fluidity ceases. This must not be taken too literally. Pour point does not denote the temperature at which an oil ceases to flow under all conditions. Often oil will flow from a barrel below its pour point, simply because there is a hydrostatic head pushing it out. Similarly an oil can be transported through a pipe if there is sufficient force behind it. The danger arises when a pump is employed to lift the oil. The pump may be powerful enough to do all that is necessary on the pressure side, but is incapable of raising the oil due to cavitation and air rushing in. In refrigeration systems oil may be carried from the compressor to the condenser where it fouls the surface of the pipes and hinders heat transference. Clearly the oil must have a sufficiently low pour point to enable it to flow off the pipes.

Demulsification value is associated principally with turbine oils, but there is no earthly reason why it should not be applied to other oils where water contact is possible. The reduction of the demulsification value of almost any red or amber oil is possible by generous earth treatment, consequently whatever demand is made it is tolerably certain to be met. That is with a new oil. But new oil can very quickly become used oil, and what was good may rapidly deteriorate. The significance of a low demulsification value of a new oil is of insufficient assurance. Naturally it is proper to start well. Unfortunately there is no recognised laboratory test by which a forecast can be made of the increase in demulsification value when the oil is in service. Many attempts have been made. The result is that a considerable amount of conservatism is observed in turbine oil production. When a sure product has been prepared little deviation is permitted. For this reason turbine oils are in a special classification. After a good turbine oil has been installed demulsification values do on occasions rise. Sometimes the cause is obscure. Before condemning it try to analyse the risks of keeping it in. It would be a great pity to cast it out if the hazards are small and can be kept under proper surveillance.

Steam engine crank-case oils are prone to contamination with water, therefore demulsification value must be considered in their case. Cautious thinking is desirable before extending the test to all cases where water is a likely entrant. Diesel engines at sea may gather water, but as diesel oils very quickly develop a high demulsification value one can only hope that the water will be withdrawn before trouble arises. A little emulsion may be harmless even if it is allowed to circulate. Emulsion troubles usually arise when the emulsion is too viscous to circulate or when it is inadequate to provide lubrication.

Acidity in mineral oil is almost negligible. One or two cheap dark oils possess acidity, but for the purpose where they are used it is of little consequence. Fatty oils are different. In them the acidity may be anything, and must be determined. What the upper limit can be depends upon circumstances. It is exceedingly difficult to offer much help in arriving at a figure. Neatsfoot oil normally has an acidity of about 1 per cent, firsts castor oil rarely exceeds 1·7 per cent, whereas bone oil may be 10 per cent. The upper limit is frequently fixed by the availability of supplies. Free fatty acid can inhibit and induce rusting, it can tarnish copper and it can brighten it. Hence before condemning an acid oil ascertain whether it has been carefully or carelessly prepared. It is common practice to add small quantities of oleic acid to a mineral oil to increase oiliness. Minute quantities of acid at elevated temperatures can cause serious pitting of cadmium alloy bearings, and there are cases where copper-lead bearings have pitted, but in other cases they have been immune from attack.

Acid development is an aspect different from free acidity in new oil. Oxidation of both mineral and fatty oils gives rise to free fatty acids. So far there does not appear to be any means for checking the development in fatty oils except the usual ones of reducing aeration, lowering the temperature, removing as far as possible metals with pro-oxidant properties. For mineral oils inhibitors are available. They may reduce oxidation or render the metal surface free from attack. Among the inhibitors may be mentioned phenyl-α-naphthylamine, β-naphthol and tertiary butyl cresol, and among the protectors are tributyl phosphite and mercaptobenzothiazole. Apart from the turbine, air compressor, and transformer oils, there is little need to be worried about acid increase. The chief anxiety about acid is, of course, its corrosive property.

Oxidation is so closely allied to all forms of oil deterioration that it has become recognised as one of the most important items in oil technology. Unfortunately it is one of the least understood problems. Much effort has been expended upon it, but still a good test is wanted, and interpretation of present methods improved. With all these shortcomings, oxidation tests serve a useful purpose. The sludge or oxidation test for transformer oil is still held to be a direct measure of the liability of an oil to deposit sludge in an electrical transformer. Also it is a good guide to sludge troubles in machines where the oil temperature is not very high. The British Air Ministry has extended the simple air blowing by noting the difference between the coke value before and after blowing. By this test it judges the suitability of an oil for petrol aero engines. Should this test be utilised for petrol engines in general it may be desirable to modify the standards upon which assessment is made. In tests of this kind a price factor may be a serious consideration in controlling the standard demanded. The author's method of heating oil in a petri dish with iron filings has given useful data. Oxygen absorption methods have been advocated, but it is well to leave them out until more definite pronouncements have been made.

Oxidation inhibitors have upset oxidation tests, consequently special care should be exercised if their presence is suspected. Metal soaps do definitely show good results in an internal combustion engine, but often increase the oxidation value. On the other hand some chemical addition agents reduce the oxidation value and increase deposits in engines.

Whilst it would be safe to generalise that oils operating at high temperatures in air require low oxidation values, it would be unsafe to conclude that when low temperatures are encountered a high value is permissible. Watch oils are called upon to provide service for long periods, and any sludge formed would throw a good deal of extra work on the delicate mechanism, resulting in bad timing and stopping.

Carbon residue test was advanced to gauge the amount of carbon formation in the combustion space of petrol engines. It still has many adherents, but it has also many opponents, the reason being that it is dependent upon the make-up of the oil. Straight run distillates have comparatively low values, but when they are blended with cylinder stocks up goes the figure. Consequently it resolves itself into an argument whether to use distillates or a blend. Clearly a middle course must be steered. For low viscosity oils a low value is obtained, but for higher viscosities there is a choice of using a blend rich or poor in cylinder oil. Which blends or distillates to use is a long story, and not easy, therefore it is probably better to follow the line of least resistance and listen to the arguments of the respective companies.

Hard asphalt determination need only be done on dark coloured oils. Suffice it to say that in general the better class oils contain the least.

For years there have been arguments about sulphur in lubricating oils, and still differences of opinion exist. Possibly they will continue to exist as long as good quality oils can be obtained from crudes which are naturally low in sulphur, and oils with a relatively high sulphur content are behaving satisfactorily in service. It might be a little imprudent to ignore the sulphur entirely whilst feelings run high, but it can safely be predicted that the protagonists for low sulphur are propelled by a wave of caution. The active sulphur compounds are easily removed in refining operations. Those compounds which elude the refiner's art are stable, and not very likely to be sufficiently active to cause serious damage in service. The fears that sulphur compounds accelerate oxidation have often been created by the knowledge that oils containing considerable quantities of sulphur have high oxidation values. Evidence that the susceptibility to oxidation is due to the sulphur compounds is lacking—it might be entirely due to the general construction of the hydrocarbon family.

With the introduction of sulphured oils for cutting, sulphur compounds for hypoid gears and sulphur compounds as anti-oxidants, the situation has become doubly difficult.

Mechanical testing covers a big area. It includes extreme pressure machines, gear tests, coefficient of friction, and any device which may be conceived to secure knowledge on any aspect. Such tests are often of inestimable value, provided always that they really do bear some relation to the main issue. Warning should be given that surface condition plays an overwhelming part in lubrication problems. Many results have been rendered useless by not paying sufficient attention to this one factor.

CHAPTER VIII

TESTS

Prior to 1920 the testing of petroleum products was in an unsatisfactory condition. Everybody was free to use whatever method they wished, and any apparatus they preferred. The result was that a good deal of confusion existed, and many unorthodox tests were suggested. The Institute of Petroleum, or Institution of Petroleum Technologists as it was called in those days, felt that some standardisation of tests should be undertaken. The task was not simple at first, but by tactful handling it won through, and a set of standard methods was published. In March 1944 the fifth edition of *Standard Methods for Testing Petroleum and its Products* was published. This book contains a comprehensive set of tests exceedingly well written, and has the advantage of being constructed by the leading men in the industry, supported by other experts. These tests have been accepted by all who are interested in petroleum, therefore it is imperative that all newcomers to the subject shall follow the lead.

In the U.S.A. the American Society for Testing Materials issues annually the *A.S.T.M. Standards on Petroleum Products and Lubricants.*

These two publications are not strictly identical, but wherever possible the two institutions agree upon the same details. The differences are not necessarily due to variations of opinion, but more to local conditions. There is, however, a very close co-operation between the A.S.T.M. and the Institute of Petroleum. All the standard methods given in this chapter are taken from these two books, though much of the detail is omitted for the sake of brevity. Any explanations given or supplementary notes are the author's opinions.

Suitable thermometers for the various tests are recommended in *Standard Methods.* It will be found useful to employ these thermometers, as they have been carefully chosen.

Acidity. The presence of free mineral acid in petroleum oils is so rare that it is almost unnecessary to look for it. Years ago when the methods of refining were less perfect it certainly was prudent to look for traces of sulphuric acid.

Free fatty acids are always found in lubricating oils, whether they be pure mineral oils or compound with fatty oils. In unused refined petroleum oils the quantity is invariably negligible. When fatty oils are present, or in the case of used oils, the acid content should be determined. There are a few unrefined mineral oils on the market which are acidic. As these oils are used only for rough jobs the free acid is of little consequence.

Both the inorganic and the organic acidities are expressed in milligrams of potassium hydroxide required to neutralise one gram of oil.

The determination of total acidity is made by weighing accurately about 10 grams of oil in a small flask, adding about 50 ml. of neutralised 95 per cent alcohol and 1 ml. of phenolphthalein solution (5 grams in 1 litre of alcohol). The mixture is boiled on a hot plate or water bath for 5 minutes, and agitated by swirling to extract the free acids. When the solution has cooled to 40–50° C. it is titrated with 0·1 N potassium hydroxide solution.

From time to time alkali blue has been suggested as an alternative indicator to phenolphthalein, but it has not received very much support.

Recently, however, it has been shown that alkali blue is really an excellent indicator provided certain precautions are taken in its preparation. It is now accepted as a Standard Method reagent. Two gm. of alkali blue are thoroughly extracted with boiling alcohol in a Soxhlet, if one is available. The solution is filtered, if necessary, and then made up to 100 ml. with alcohol.

When alkali blue is used 10 gm. of the oil sample is dissolved in a mixture of 3 volumes of benzene and 2 volumes of alcohol. The solvent should be neutralised before the oil is dissolved in it. This is done by adding about 2 ml. of alkali blue solution, and one drop of acid which sensitises the alkali blue. The mixture is then neutralised with potassium hydroxide. Apparently this sensitisation is the real secret of success with alkali blue. The end point is very much more distinct even with used oils.

The inorganic acidity is determined by extracting about 100 grams of oil with 100 ml. of warm distilled water, neutralised if necessary. The mixture is well shaken, and titrated with 0·1 N potassium hydroxide solution in the presence of 0·1 ml. of methyl orange solution (1 gram in 1 litre of distilled water). It will be found easier to see the end-point if the aqueous layer is separated from the oil in a separating funnel.

The organic acidity is found by subtracting the mineral acidity from the total acidity.

With pale oils it is usually easy to observe the end-point, but with red or black oils it is more difficult, particularly in a bad light. Used oils often call for much consideration and care, as the end-point is vague. Different observers may report what look to be material differences, but it is well to bear in mind how many drops of alkali are involved, and how important the result may be. To safeguard the operator he may wish to append the saving clause "end-point vague." Such a clause is understood and protective, but it should not be utilised merely as a screen for poor manipulation. There is very little excuse for it being applied to unused oils. Sometimes difficulty is encountered by the pink colour fading after a few seconds, and repeatedly fading after subsequent additions of alkali, particularly when the mixture is violently shaken. This is due to alkali attack upon easily reactable material in the oil. How to deal with this difficulty has not been settled, but the obvious course is to follow the manipulation detail meticulously and ignore subsequent reactions.

Investigators have turned their attention to electrometric methods, but so far no satisfactory procedure has been accepted.

Fatty oils offer no particular difficulties. Oils with high acidity may require a smaller test sample, but this is purely a matter of convenience. How the acidity shall be expressed is dependent upon trade practices. It can, of course, be expressed as milligrams of potassium hydroxide required to neutralise one gram of oil, or in terms of oleic acid expressed as a percentage by weight.

The acidity of petroleum jellies is sometimes materially higher than of petroleum oils. The conclusion may be reached, therefore, that they are corrosive. If so, pause, and seek corroborating evidence; often it will be found to be lacking.

The procedure for the estimation of free acid in greases is different from that for oils. 10–30 grams of grease is weighed in a small beaker and mixed thoroughly with 75 ml. of petroleum spirit. The whole is transferred to a 250 ml. Erlenmeyer flask with the aid of a further quantity of spirit, and the beaker washed with 50 ml. of neutralised alcohol, using a small quantity at a time. The alcohol washings are added to the flask, and the mixture well shaken. About 1 ml. of phenolphthalein solution is added. If it is colourless it is titrated with 0·5 N alcoholic potassium hydroxide in the cold. The reason for using alcoholic alkali is to avoid splitting of the soap by water. The result is expressed as the number of milligrams of potassium hydroxide required to neutralise the acidity of 1 gram of the grease.

The method is not applicable to greases containing iron, zinc, aluminium and certain other metallic soaps. It is suitable for calcium and soda soap greases. Used greases may cause difficulties; when they do it is prudent to record the fact.

Aniline Point of an oil is the lowest temperature at which the oil is completely soluble in an equal volume of aniline. Apparently its only real practical value with lubricating oils is to ascertain its probable action on natural rubber It is too early yet to indicate how far it is applicable for synthetic rubbers, most of which are tolerably resistant to mineral oils. Clearly the best test is to immerse the particular rubber in the oil and observe any swelling or softening which occurs, but this may involve many weeks; therefore, a quick test to obtain probabilities is desirable.

A little preliminary work is necessary. The aniline used must be of A.R. quality. It must be carefully dried over solid potassium hydroxide, filtered, and re-distilled, the first and last 10 per cent being discarded. During the drying it should not be left in contact with the potassium hydroxide for more than 24 hours, nor should the re-distilled aniline be used if it is more than 7 days old without re-purification.

The oil sample must be dried either with anhydrous calcium chloride or anhydrous sodium sulphate. After drying the oil is decanted or filtered. If any wax crystallises at atmospheric temperature the oil is warmed to re-dissolve the wax.

Before commencing the test the apparatus is assembled and dried at 100–110°C. The apparatus consists of a test tube, 25 mm. × 150 mm., supported centrally in a jacket tube 38 mm. × 150 mm., and a stirrer conveniently made from wire or glass rod with a ring about 15 mm. in diameter at the bottom; 5 ml. of the dried oil and 5 ml. of the aniline are measured into the test tube. The oil can be measured by an ordinary pipette, but the aniline should not be sucked up by the mouth owing to its toxicity but by a suction bulb and aspirator. The tubes are suspended in a heating bath, the inner tube is adjusted to within 20 mm. of the bottom of the jacket tube, and the thermometer is held centrally in the tube with the bulb 5 mm. from the bottom.

If a homogeneous mixture is not formed at atmospheric temperature it is heated, and stirred vigorously, but avoiding splashing and aeration as far as possible, until complete miscibility is obtained. The apparatus is withdrawn from the bath and allowed to cool at a rate not exceeding 1°C. per minute with constant stirring. The temperature at which the mixture becomes so cloudy as to obscure the thermometer bulb in reflected light is recorded as the approximate aniline point.

ANILINE POINTS

Conventionally refined	Aniline Point
1	90° C.
2	72°C
3	85°C.
Solvent refined	
4	98°C.
5	104°C.
Bright stocks	
6	123°C.
7	114°C.
8	126°C.

Any particular set of observations upon the effect of oils upon natural rubber is not necessarily true for all types of natural rubber, but in view of the growing applications of rubber in contact with oil, laboratory obtained results may be sufficiently indicative to be useful.

Oil	Days immersed	Increase in weight
Transformer .	19	32%
DTD 44B . .	19	42%
Castor . . .	71	1%
Linseed . .	71	112%
Groundnut . .	71	48%
Rape . .	71	71%

It is often alleged that the action of mineral oil on rubber diminishes with increase of viscosity. This may be misleading because the high viscosity oils have less ability to penetrate, so on a time basis there may be some justification for the belief. Should sufficient time be allowed, swelling will doubtless occur. Rubber which is highly vulcanised or heavily loaded will behave somewhat differently.

Recently introduced synthetic rubbers are alleged to be unaffected by oil. Such a statement is relative, and not necessarily equally true for Buna and Neoprene.

Ash. Before chemical additives were used in lubricating oils it was only neecssary to burn a known quantity of the oil in a silica basin and weigh the ash. Now a little more consideration must be given, because sometimes there may be present zinc, lead, chromium, tin, barium or aluminium compounds. Organo-metallic compounds are extensively used in petrol, diesel and gear lubricating oils. Should zinc or lead be present, direct incineration cannot be applied as some of the metal would be lost by volatilisation. In such cases the oil is partly boiled off by heating until the vapours ignite, and allowing them to burn until the oil has nearly disappeared. After cooling, strong sulphuric acid is added, heated carefully, and digested at a gentle heat until the oil has been completely oxidised, and the zinc or lead converted into sulphates. Sometimes it is considered safer to digest the original oil with strong sulphuric acid in a Kjeldahl flask until the oil has been oxidised. The sulphuric acid is evaporated with great care and the sulphate residue weighed. Should there be any carbonaceous matter contaminating the sulphates it should be burnt off at as low a temperature as possible, then the residue is wetted with strong sulphuric acid to reconvert the ash to sulphate. The acid is removed by evaporation, with the aid of a little ammonium carbonate. Ammonium carbonate is easily destroyed by gentle heat, and the ammonium sulphate is also readily decomposed.

When zinc or lead are present the oil must not be burned in a platinum dish, as the platinum is sure to be attacked.

Chromium and tin do not complicate the determination of the ash by ordinary incineration, but if they have to be determined separately afterwards, too high a temperature should be avoided otherwise they are rendered very insoluble. Even after careful incineration it is necessary to fuse the ash with fusion mixture and sodium peroxide to make it soluble in acid.

In the event of water being present in the oil, foaming and spitting are liable to occur. These troublesome happenings can often be stopped by adding a few drops of absolute alcohol before heating. The alcohol absorbs the water if stirred into the oil, and may then float on the surface, and burn quietly. Should it be unsuccessful a mixture of benzene and alcohol may be better, particularly if one or two strips of ashless filter paper are inserted in the mixture.

The quantity of oil to be taken for the ash content depends upon the ash content. Usually it is between 20 and 50 grams.

When determining the ash content it is well to keep in mind the possibility that it may be necessary to make a quantitative analysis of it, consequently nothing should be done which may render it more difficult.

Asphaltenes (Hard Asphalt) are the wax-free materials insoluble in petroleum spirit which are soluble in benzene. The solubility of the material in benzene is important. This test should be reserved mainly for new oils. Reference to used oils will be made in a subsequent paragraph.

Not more than 10 grams is weighed in a conical flask and ten times its weight of petroleum spirit added, thoroughly mixed and kept in the dark for 18–23 hours. A cork is put into the flask to check evaporation of the spirit.

It is important that the quantity of asphaltene separated shall be approximately 0·25 grams, therefore it is prudent to weigh out at least three separate lots each having different weights, in the hope that two of them will give the desired amount of asphaltene.

The colloidal asphaltenes are flocculated by the spirit and precipitated. The supernatant liquid is decanted through a good filter paper, and the precipitate is very well washed in the usual way with further quantities of the petroleum spirit; this time the spirit is hot. Finally the whole of the precipitate is transferred to the filter. Sometimes the precipitate is difficult to wash. In such cases it is convenient to wash it as far as possible in the flask, and delay its transfer to the filter.

The next step is to remove any wax which might be present. This is done by washing the precipitate with boiling 95 per cent alcohol. Obviously this can best be done in the flask. The washings are passed through the filter. The washing is continued until no residue is left on a watch glass when the filtrate is evaporated.

The residue is then treated with hot benzene to dissolve the asphaltenes. The benzene solution is passed through the filter into a weighed flask. Several treatments with benzene are necessary to ensure complete solution. The benzene is distilled off on a water bath, and the residue dried at 100–110°C. for two hours with occasional removal of the vapour in the flask by a current of air. Any vapour remaining in the flask should be removed immediately before its final removal from the oven. The asphaltenes are weighed.

For used oils there is no standard method, although if asphaltenes are reported it is reasonable to determine them by the method just given. Whether asphaltenes should be reported is another matter. It seems proper to record the total insolubles in petroleum spirit, and then the portion of that which is soluble in benzene, and as a convenience the portion which is insoluble in benzene. In an engine it would appear that the total generated solids in the oil are important, as the whole of them are potential sources of trouble. The ratio of the soluble in benzene to the insoluble in benzene is often useful as a basis of comment on the solids formed. Further reference to this subject will be found in the chapter on deposits. The amount of ash in the oil must be determined.

The I.P. petroleum spirit used for unused oils must conform to the standard specification. The principal features are that 90 per cent shall distil between 60–80° C., that its aromatic content shall be under 0·5 per cent, and its aniline point is 58–62° C.

Probably many chemists will prefer to use this spirit for used oils, although a spirit which distils under 40° C. gives more accurate results, and higher results. The I.P. spirit is fairly easily obtained, but the under 40 spirit may not be stocked everywhere, consequently supply may govern the choice.

Carbon Residue has long been associated with the name of Conradson in the U.S.A., and in this country with Ramsbottom. Conradson's method was subjected to much criticism years ago on the grounds of poor repeatability. Since then the method has been made more precise, but even now it cannot be considered to give a better repeatability than 10 per cent. Too much attention should not be given to a test unless it can be shown that the inference from the test demands a high degree of accuracy. The test is only intended to throw some light on the relative carbon-forming propensity of an oil. It does not claim anything more. It is a relative test. Ramsbottom was not sufficiently satisfied with the Conradson method to include it in the British Air Ministry specification for aircraft oils, so he suggested a modification which gives a better repeatability. In principle both methods are the same. They both aim at distilling off the oil in an air-free atmosphere and collecting the residue. Since the residue only contains about 1·5 per cent of combined oxygen it can be accepted that very little oxidation occurs. The carbon residue is the resultant product of heat. During the distillation the air is expelled from the container by oil vapour, but when all this has gone air is free to return and oxidise the carbon residue, consequently the heating must be stopped after a predetermined time. Further, the temperature must be controlled as accurately as possible. A sufficiently high temperature is necessary to ensure complete distillation of the oil, but insufficiently high to encourage burning of the carbon residue. Ramsbottom lays great stress upon the maintenance of a uniform temperature, and provides the means for doing it, whereas Conradson relies upon a less exact method.

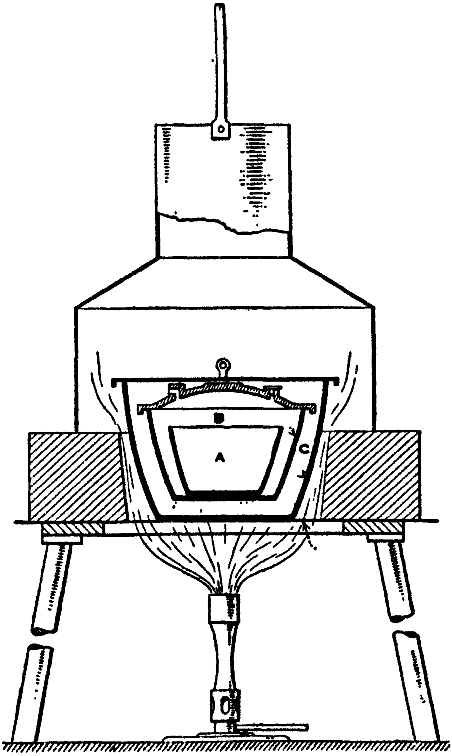


Fig. 6.—Apparatus for determining carbon residue.

Crucible A.—Porcelain crucible glazed throughout. Capacity 29–31mm. Rim diameter 46–49 mm.

Crucible B.—Iron, flanged and ringed. Capacity 65–82 ml. Diameter of flange 53–57 mm. inside, 60–67 mm. outside. Height 37–39 mm. Cover without delivery tubes, and vertical opening closed. Horizontal opening to be kept clean. Diameter of flat bottom 30–32 mm. outside.

Crucible C.—Spun sheet iron. Rim diameter 78–82 mm. outside. Height 58–60 mm. Thickness 0·8 mm.

Conradson Method. Two glass beads about 0·1 inch in diameter are placed in and included in the weight of a tared porcelain or silica crucible, into which 10 grams of the oil, free from moisture and suspended matter are weighed. The crucible is placed in the centre of a Skidmore crucible, which rests on a layer of about 25 ml. of sand in an iron crucible fitted with a loosely fitting lid to allow free exit to the oil vapour.

The outer crucible is rested upon a nichrome wire triangle, surrounded by the insulator and covered by the hood. Then heat is applied by a good Meker burner, 1 inch in diameter and 6 inches in height, so that the pre-ignition period will be $10 \pm 1{\cdot}5$ minutes. More rapid heating may cause foaming of the oil. When smoke appears above the chimney tilt the burner to ignite the oil vapours. The burner may be removed for a few moments for the flame of the oil vapour to adjust itself to be between the top of the chimney and the top of the bridge on the chimney. When the vapours are burning steadily at this height the gas flame is restored and adjusted to maintain this uniform rate of burning. The burning period should be 13 ± 1 minutes. The burning time is important.

When the vapours cease to burn, and no further blue smoke can be observed, the heat is increased to its original intensity for exactly 7 minutes, so as to make the bottom and lower part of the large crucible a cherry red. The total period of heating shall be 30 ± 2 minutes.

Allow to cool for about 15 minutes, remove the hood and transfer the porcelain crucible to a desiccator, cool, and weigh. Calculate the percentage of carbon residue on the original sample.

Ramsbottom Method. A hard glass tube $25 \pm 0{\cdot}4$ mm. in diameter and 1 mm. thick is drawn out at one end to a capillary of $1{\cdot}5 \pm 0{\cdot}1$mm. internal diameter and 9·5 mm. in length. The other end of the tube is rounded. The distance from the base to the shoulder of the bulb is 38 mm., and the overall length from the base to the tip of the capillary is 57 mm.

Into the bulb is weighed $4{\cdot}0 \pm 0{\cdot}1$ grams of oil. The oil can be introduced by inserting a fine glass tube, suitably bent, into the capillary and applying suction while the end of the bulb is immersed in the oil. The bulb is then placed in an iron sheath closed at one end 76 mm. in length and approximately 25·5 mm. in diameter, and about 1 mm. in thickness. The sheath is immersed in a lead bath to a depth of at least 73 mm. To ensure uniform heating of the bulb the weight of lead in the bath should be about 56 lb., and the bottom of the sheath should be about 25·4 mm. off the bottom of the bath. It is absolutely essential that the iron pot shall be strong and not liable to crack. An ordinary household iron pan is dangerous. A convenient vessel for holding the lead is a large round bottomed iron solderer's bath, fitted with a lid. Considerable oxidation of the lead occurs when it is hot. The lead oxide should be removed periodically, and more lead added to maintain the level. A certain amount of care is necessary when inserting the bulb into the hot sheath if fracture of the glass is to be avoided.

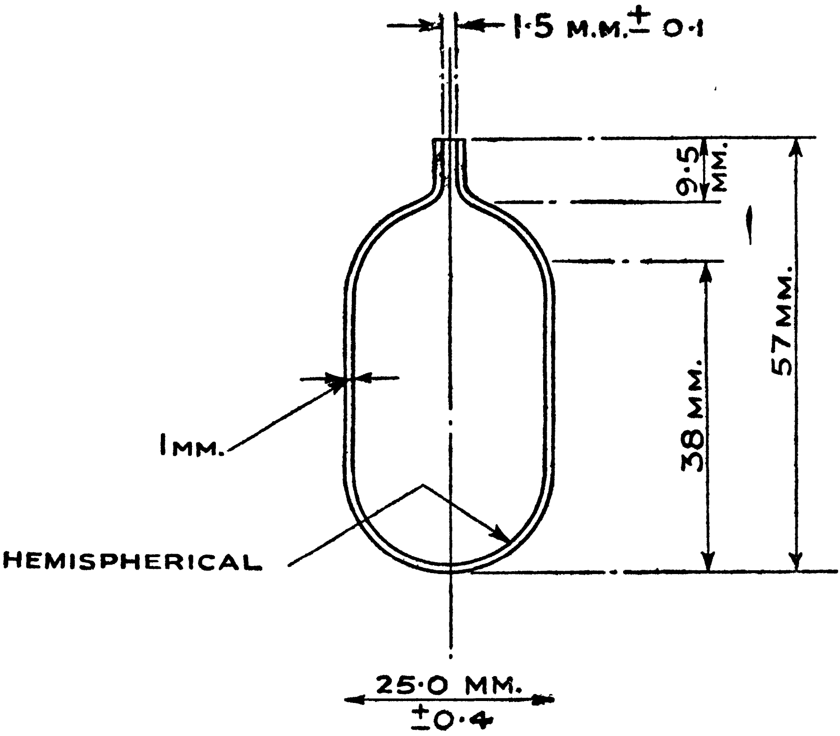


Fig. 7.—Ramsbottom Coking Bulb. 5 per cent on all dimensions permitted except where otherwise stipulated.

The lead bath needs an ample gas burner to heat it to 550 ±5° C. The temperature is measured by a reliable pyrometer, which has been accurately calibrated, and which is frequently checked. The accuracy of the pyrometer is essential. The stem should be protected by a silica or thin metal sheath against the attack of the lead on the wires. Precautions must be taken to protect the recording instrument from the heat of the bath. The connecting wires cannot be wholly shielded, but by inserting the pyrometer obliquely and supporting the covered wires away from the pot, burning can be obviated. The end of the pyrometer sheath should be 1 inch from the bottom of the bath.

It is prudent to do the tests in duplicate. A bath of this size will hold four bulbs. The bulbs should be inserted simultaneously, and if there is any drop in temperature it must be readjusted. On heating the oil it will distil, and the vapours ignite. After 20 minutes heating the bulbs are withdrawn with crucible tongs, cooled for 15 minutes in air, and finally in a desiccator, then wiped and weighed.

The apparatus should be checked occasionally by carrying out a determination on an oil of known Ramsbottom carbon residue.

Should it be difficult to obtain a supply of new bulbs, those which have been used can be cleaned by burning off the carbon in an atmosphere of oxygen. The Ollett cleaner is a convenient apparatus for this purpose. It can be purchased from laboratory furnishers.

Cloud and Pour Points. The cloud point is only intended for use on oils which are transparent in layers 1½ inches in thickness, but the pour point is intended for all petroleum oils.

The two tests, although made in the same apparatus, are not comparable. Cloud point is obtained to ascertain the temperature at which paraffin wax begins to crystallise or separate from solution when the oil is cooled under prescribed conditions. It is of interest to pharmacists who expose medicinal paraffin in their shop windows, but with lubricating oils which are available to-day it has little interest to users. Certainly there is little useful purpose to be served by including it in lubricating oil specifications.

Pour point is quite different—it is of considerable value, but open to criticism. Pour point is the lowest temperature at which an oil will flow when cooled under prescribed conditions. The words "under prescribed conditions" do cut away the criticism. It is wrong to believe that an oil cannot flow below its pour point, because it can. It can flow out of a barrel if the hole is large enough; it can flow through a pipe if the pressure exceeds the viscous resistance.

A number of tests have been suggested under various names to describe the cold tests of oils. Some of them may have distinct advantages for specific needs, some may give better reproducibility, but unless any one can show a vast improvement upon the standard pour test it will have little chance of survival against the test which is now virtually international.

The apparatus is simplicity itself, consisting of a cylindrical test jar with flat bottom, 30–33·5 mm. inside diameter and 115–125 mm. in height. To assist even cooling the test jar is jacketed with a wider tube 115 mm. in height and 9·5–12·5 mm. greater in diameter than the test jar. A disc of cork or felt is placed between the bottom of the test jar and the jacket, and a distance ring of cork or felt about 5 mm. thick keeps the test jar in position. The thermometer is inserted through a cork into the test jar so that the bulb rests on the bottom. This assembly is suitably supported in a cooling bath of optional size.

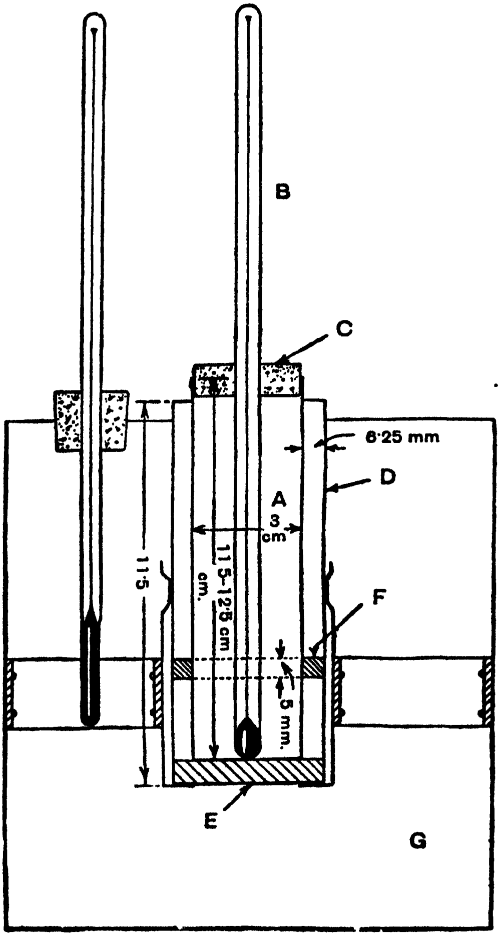


Fig. 8.—Cloud and Pour Points.

For a cloud point determination the oil is dried by passage through dry filter paper until perfectly clear at a temperature at least above the cloud point. Into the test jar is poured the oil to a depth of 51–57 mm. It is important that the inside of the jacket shall be clean and dry. The next important factor is the cooling. First the assembly is inserted into a cooling medium at 30–35° F. so that only about one inch of the jacket projects above the liquid medium. As the cooling proceeds the test jar is withdrawn quickly, but without disturbing the oil, at every 2° F. fall and examined for cloud, and replaced all within 3 seconds. If no cloud appears when it reaches 50° F. it is transferred to a second cooling bath at 0—5° F., and cooled and examined as before. Should there be no sign of cloud at 20° F. it is transferred to a third cooling bath at —30 to —25° F. The first distinct cloudiness or haze in the oil at the bottom of the test jar is regarded as the cloud point.

For the pour point determination proceed as for cloud point, but before cooling the oil shall be heated without stirring to 115° in a bath at 118° F., then cooled in air to 90° F., or 60° F. if the pour point of the oil is below —30° F. Cooling is as before, but instead of withdrawing the test jar at every 2° F. it is withdrawn at every 5°. When the jar is withdrawn it is tilted to ascertain whether the oil is still fluid. As soon as the oil ceases to flow the jar is held in a horizontal position for exactly 5 seconds. If the oil shows any movement under these conditions the test jar is immediately replaced in the jacket and a test for flow repeated at the next temperature 5° F. lower. The pour point is taken as the temperature 5° F. above the temperature at which it just ceases to flow.

At no time should the test jar be placed directly into the cooling bath.

Pour points of some black oils are sometimes very indefinite. A special procedure has been suggested in Standard Methods, but it does not really overcome the difficulty, it only alleviates it. Those who have had experience with these classes of oil are not happy with the results obtained, consequently, the less experienced may be advised to accept that the pour point is indefinite.

Demulsification Value is an important consideration in judging the suitability of turbine and crank chamber oils. Into turbine oil reservoirs and crank chambers there is frequently a leakage of water, which becomes mixed with the oil, and if it does not separate readily, gives rise to emulsions, thereby diminishing the value of the oil as a lubricant, in addition to the risk of choking the feed pipes. Furthermore, as it is imperative to remove the emulsion formed, a quantity of oil is lost in the emulsion; if the emulsion is much, the loss of oil through this medium becomes considerable. Emulsions may be troublesome by carrying salts from the water through the lubricating system, and causing corrosion, and excessive sludging of the oil. They can set up an e.m.f. between the bearing and the journal.

The power of an oil to form an emulsion with water may be due to several conditions. Stable emulsions can be made, using emulsifying agents which are known not to have any marked effect on the surface tension of water. This is important, because it was believed that soaps and other substances which would reduce the surface tension of water were chiefly responsible for the production of emulsions, whereas it is known that colloidal ferric oxide, which has practically no effect on the surface tension of water, is an excellent emulsifier. Pickering (*J.C.S.*, 1907, 2001) stated that the emulsifying power of a solid substance depends solely on the size of the particles constituting it, provided it is wetted more easily by water than by oil. This, however, is not always true, for if basic sulphates, clays, etc., which will form emulsions, be dried and very finely powdered, no emulsion will result. Not only, then, does the emulsifying action of insoluble particles depend on the fineness of division, but it must also be of such a nature and in such a state that it can, and does, form a coherent film around the globules of oil.

For many years the demulsification value has been expressed in minutes and half-minutes. Now it is to be expressed in seconds. The sudden change from a few units to many units may cause some embarrassment to those who have grown accustomed to the old style, and create alarm in the minds of engineers, particularly when the figures exceed 600 for used oils. Doubtless any discord will be short-lived. So, too, it is hoped that the old expression, 20 plus, or its new equivalent, 1,200 plus, will no longer be regarded as a distinctive barrier dividing something material from something mystical. Actually, it simply denotes the point at which the apparatus fails to produce intelligent results. Any desire to press for results beyond the limit of the apparatus should, therefore, be suppressed.

The apparatus consists of a steam generator, a steam delivery tube (internal diameter 2·3–2·7 mm.), with the open end ground off to an angle of 30°, and a graduated test tube. To ensure a uniform size of steam bubble, uniform stirring, and a uniform height of oil and water during the test, standardised dimensions of the essential parts are necessary. The standard test tube has a length of 200 mm., internal diameter of about 23 mm., and is graduated from 0 to 50 ml. or from 10 to 50 ml. in millilitres. The distance from the 10 ml. line to the 50 ml. line should not be less than 93 mm. nor more than 103 mm. For easy reading, each 5 ml. line encircles the tube. Two beakers are provided, each of 3–3·5 litres capacity and 19–23 cm. deep. They are fitted with wooden covers, through which two holes are drilled for passing the test tube and a thermometer. Wooden covers often curl badly, therefore it is more convenient to employ stout aluminium or plastic sheet. The beakers are nearly filled with water at a temperature of 67–70° F. and 200–203° F., respectively.

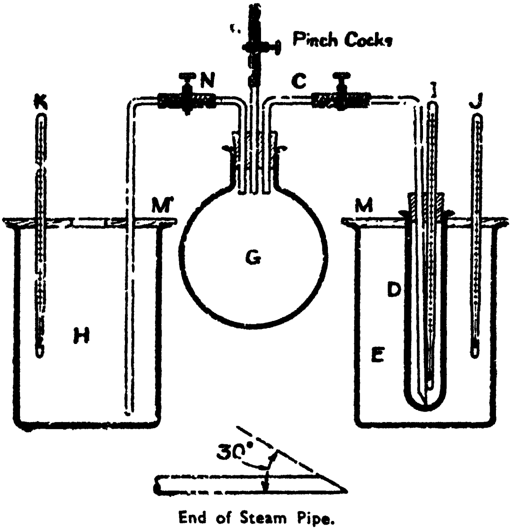


Fig. 9.—I.P. Demulsification.

20 ml. of the oil to be tested is placed in the test tube, which is suspended in the beaker containing water at an initial temperature of 67–78° F. Steam from the generator is made to pass through the delivery tube until condensation in the tube ceases, then it is inserted into the oil until it rests on the centre of the bottom of the test tube. It is maintained in the correct position by a cork in the top of the test tube. The cork also carries a thermometer, whose bulb is 20–25 mm. from the bottom of the oil container. Steam is admitted at a rate which will maintain the temperature of the oil between 190–195° F. Usually the necessary temperature is reached

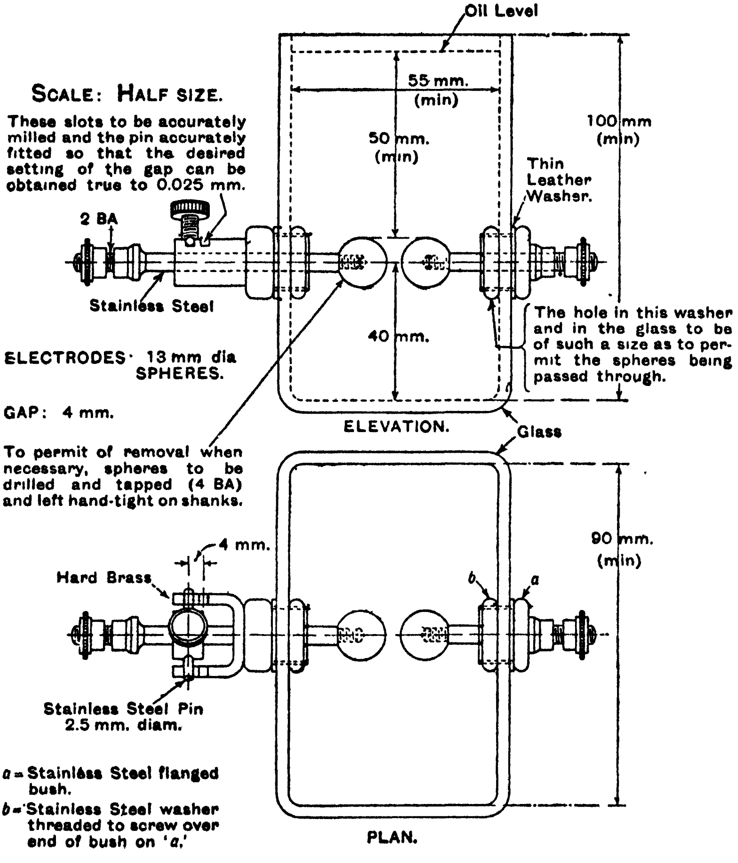
in 45–75 seconds. To allow steam to escape, a narrow channel is cut out in the side of the cork. The steam jet violently agitates the oil, and at the same time steam condenses into water, which becomes intimately mixed with the oil. When the volume of oil and water reaches 40+3 ml. the steam tube, thermometer and cork are withdrawn, that is, after 4–6·5 minutes, and the test tube is transferred to the other large beaker. It is extremely important that this beaker of water is maintained at 200–203° F. Immediately the steam tube is withdrawn, a stop watch is started to measure the time taken for the oil and water to separate.

With oils which have a low demulsification value no difficulty ever seems to arise about a definite value. When the value exceeds 600, an indeterminate layer sometimes does form, which may give rise to a little difficulty. As the demulsification value measures the time for the separation of the oil and water, too much notice need not be taken of the emulsion lattice which forms in the aqueous layer. Fortunately, this difficulty does not arise with new oils of appropriate quality. It will only occur, therefore, with used oils in which the exact figure is of lesser importance. It is probably true to say that the demulsification of any used oil should be regarded as somewhat approximate.

Dielectric Strength is of importance in judging the insulating value of transformer and switch oils. It indicates the presence of moisture and fibres, but it does not measure them. The test is useful for detecting small quantities of water, therefore it can be used for any oil which must be very dry.

As the impurities being looked for are in small amounts, considerable care should be taken in obtaining the sample. A convenient method is to allow the barrel or other container to stand for 24 hours with the bung or stopper uppermost, then a glass tube is inserted, with the upper end closed with the thumb, until it reaches the bottom of the container. The thumb is removed and the oil sucked up into the tube, and transferred to a chemically clean and dry bottle. By this means any water, fibre or dirt is likely to be collected in the sample. With used oils the procedure will depend upon circumstances, but a little consideration will indicate whether the sample should be taken where the oil is dirtiest or where it is doing its major job, bearing in mind that the object of the test is to determine whether it is safe to keep the oil in service.

The test cell consists of a glass vessel 55 mm. by 90 mm. and 100 mm. high, fitted with two spherical electrodes 13 mm. in diameter, made of brass, with a gap of exactly 4 mm. The alternating current is supplied through a transformer so that it shall be approximately of sine-wave form, and having a frequency between



NOTE: When used, the test cell is to be stood in a thick porcelain dish or otherwise insulated from earth.
All corners and edges to be well rounded off.

Fig. 10.—Dielectric strength apparatus.

25 and 100 periods per second. The test cell should stand in a porcelain tray. Voltages up to 60,000 or 70,000 may be applied to the electrodes, therefore no risk can be permitted under any circumstances. All the electrically live parts must be enclosed, and precautions taken to prevent the unskilled from using the apparatus.

Before making a test the test cell is washed out with the oil to be tested or with oil having a high dielectric strength. The final cleaning is done by placing one of these oils in the cell to the correct height and a voltage of about 15,000 applied to the electrodes for 30 seconds to attract fibres.

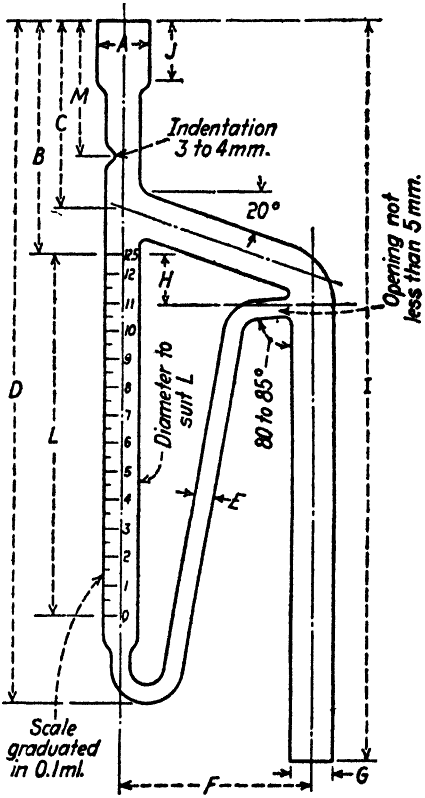
Not less than 475 ml. of the oil sample is placed in the cleaned test cell, and allowed to stand until air bubbles have escaped, and a temperature of 15·5–20° C. reached. The current is switched on, and the voltage across the electrodes steadily increased as rapidly as is consistent with the reading on the voltmeter.

There are two ways in which the result can be reported. Specifications usually specify a minimum dielectric strength, which implies that the oil shall not allow arcing between the electrodes below this value, and that when the current is maintained stationary at this voltage for 1 minute there shall be no arcing. If it is necessary to ascertain the true dielectric strength the voltage is increased until arcing occurs. Occasionally preliminary sparking takes place on a very mild scale and does not develop into arcing. Such sparks are usually ignored.

When purchasing an outfit it is well to obtain it from a firm that understands electrical methods and can guarantee that it conforms with the I.P. standards. This warning is considered to be advisable in view of apparatus which has been offered for sale to meet demands for a cheaper modification.

Diluent Content of Crank-case Oil may refer to petrol, kerosine or diesel fuel which has contaminated the lubricating oil in an internal combustion engine. Pre-dilution of lubricating oil with kerosine is resorted to in cold climates to assist easy starting, and petrol dilution of aero engine lubricating oil is sometimes practised for the same purpose. In aero engines the oil is not pre-diluted, but is added after the engine has been shut down in sufficient quantity to ease starting and to give a concentration which will enable it to evaporate when the engine starts. Under normal conditions of running some of the fuel escapes into the oil and reduces its viscosity. It may accumulate sufficiently to reduce the viscosity of the oil below a desirable degree. Dilution may also occur by flushing the engine with petrol or kerosine after draining out the used oil. Many engines possess pockets in which the flushing agent can accumulate, and from which it cannot readily escape. When new oil is added it mixes with the petrol or kerosine, and the new oil is thereby diluted. Consequently it is bad practice to flush with these materials unless the sump can be dropped, or the first lot of new oil discarded.

The method for determining the petrol content is to steam distil it, and measure the volume of petrol which condenses; 25 ml. of the oil is measured in a graduated cylinder, and transferred to a glass flask of the short-necked round-bottomed type with a capacity of



A	18 to 20 mm., inside diameter.
B	85 to 90 mm.
C	70 to 75 mm.
D	240 to 260 mm.
E	4 to 5 mm., inside diameter.
F	65 to 75 mm.
G	11 to 15 mm., inside diameter.
H	15 to 20 mm.
I	270 to 290 mm.
J	25 to 30 mm.
L	125 to 138 mm.
M	40 to 50 mm.

Fig. 11.—Diluent trap for testing crank-case oils.

1 litre. The adhering oil in the cylinder can be removed by shaking with water. Approximately 500 ml. of water is added to the flask, and the liquor vigorously boiled. The vapours are led up the side tube of a specially constructed trap into a water condenser. The condensate drops into the graduated tube where it separates into

liquid petrol and water. The excess of water in the trap returns to the flask. Before commencing the determination, the graduated limb of the trap is filled with water. Sometimes violent bumping occurs, but it can usually be subdued by broken glass, and/or the addition of 5 ml. of strong hydrochloric acid.

The bottom of the condenser is ground off at an angle of 60 degrees. The tip of the condenser should be directly over the indentation in the trap.

The separated petrol can easily be measured in the trap.

Diesel fuel oil is also determined by steam distillation, but owing to its higher boiling-point than petrol the distillation is made at a higher temperature. Although in most cases the method gives reasonably accurate results it is safer to make a steam distillation of the lubricating oil in use to ascertain whether it yields any volatile fraction under the conditions of the standard test, and to make an allowance in the test upon the used oil.

The apparatus consists of a boiler for generating steam. Any convenient vessel may be used, but it should be fitted with a blow-off tube having a valve or screw clip so that the flow of steam can be regulated. And a round-bottomed long-necked glass flask of 1 litre capacity, fitted with a cork through which passes a steam inlet tube reaching to within 1 cm. of the bottom of the flask, also a short vapour tube. The flask is immersed in an oil-bath, which can be maintained at 130° C., at an angle of about 45 degrees. The vapour tube is connected to an adequate water-cooled condenser. One with a jacket of 60 cm. and inner tube of 9·5–12·7 mm. outside diameter is preferred. Under the tip of the condenser is placed a graduated trap for collecting the distillate.

About 100 ml. of the sample is placed in the flask. The easiest way of measuring the exact volume used is to measure exactly 100 ml. in a graduated cylinder, transfer the oil to the flask, and note the quantity remaining in the cylinder after it has had time to drain from the sides. Steam is raised in the boiler, and allowed to blow through the steam line until no condensation occurs within it. If this precaution is not taken trouble will ensue when the steam line is connected to the flask. The flask containing the oil is placed in the oil-bath, already at 130° C., and left undisturbed for ten minutes to acquire the necessary temperature. Then the steam line is inserted and the vapour tube connected to the condenser, with as little delay as possible, and steam is passed into the oil at such a rate that about 10 ml. of water condensate forms per minute. The condensate of water and diesel fuel is collected in the graduated trap, which has already been filled with water. Distillation is continued until the volume of diluent passing over with 50 ml. of water is 0·1 ml.

The result is reported as a percentage by volume to the nearest 1 per cent, and it shall be stated that the value given for the diluent is only approximate, for example:

Diluent content (diesel fuel) 12 per cent vol. (approx.)

So far the Institute of Petroleum has not standardised a method for the determination of kerosine in lubricating oils. No doubt this omission will be rectified now that kerosine is being used extensively in agricultural tractors. The dilution trouble in tractors using kerosine is well known, though it is safe to assume that efforts are being made to reduce it. Kerosine cannot be wholly removed by steam distillation at 100° C., and obviously it is not necessary to heat the flask to 130° C., so some intermediate temperature must be decided upon. If 130° C. is a safe temperature for diesel lubricating oils it should be safe for kerosine engine lubricating oils which are usually higher in viscosity, but the opinion will probably be expressed that it is unnecessarily high and that 115° C. is high enough.

Flash Point of an oil is usually alluded to as the closed or open flash. It is necessary to state which flash point is meant in recording data. The open flash or flash point (open) is broadly speaking approximately 30° F. above the flash point (closed) of mineral lubricating oils. Although this may be true when an oil contains hydrocarbons of very different flash points, the flash point of a mixture of oils is not the flash point of the lowest flashing constituent, but is intermediate between the flash points of the highest and lowest flash component. By the formula of Harker and Higgins the flash point of a bi-component mixture can be calculated.

$$F = \frac{mxA + yB}{mx + y}$$

where F is the flash point of the mixture of oils whose individual flash points are A and B; x and y are the respective proportions of the two components, and m is a constant.

The flash points of fatty oils are often not sufficiently sharp and distinct to be stated precisely. Determinations are rendered difficult, due to the oil suffering from thermal decomposition and emitting a vapour of decomposition products. Free fatty acids and traces of solvent also give rise to freaky results. Flash points of fatty oils may therefore be anywhere between 300–500° F.

For American oils . . . . . m = 0·43
For Galician oils . . . . 0·91
For Russian oils . . . . 0·91

Percentage of A by volume	Flash Point of A and B	
	Found	Calculated
100	400° F.	—
80	382	380° F.
60	365	364
40	352	353
20	347	345
0	340	—

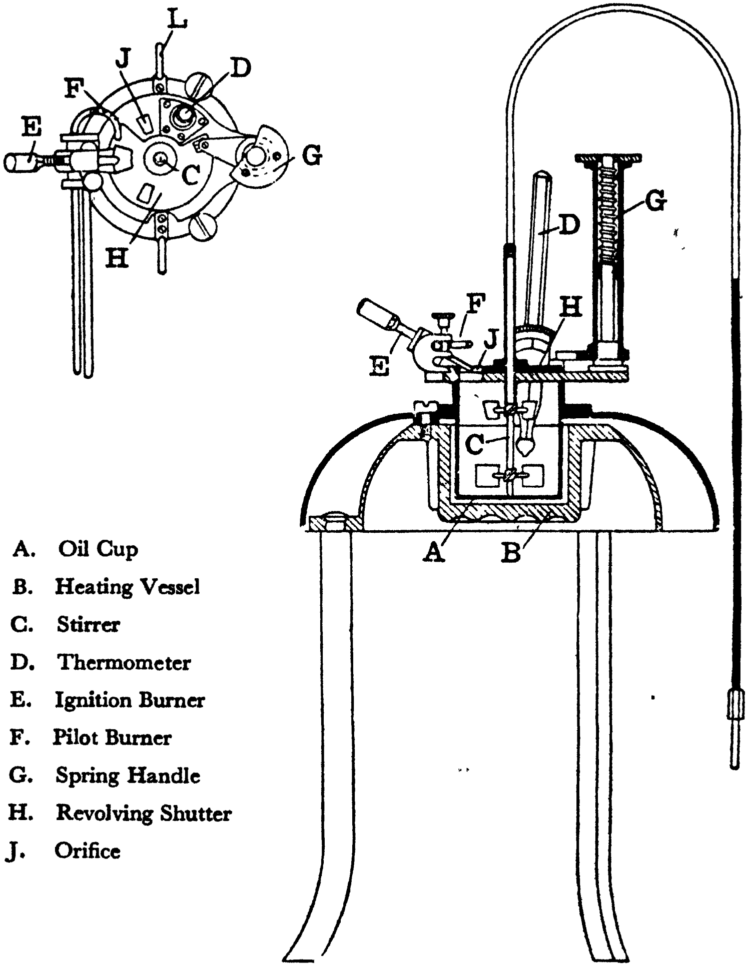
The flash point (closed) is that temperature at which the vapour from a substance will ignite in a closed vessel of definite dimensions and design. As the test is purely arbitrary some sources of error may be enumerated.

(1) frequency of application of test flame
(2) variations in the time of opening the shutter
(3) variations in the rate of heating
(4) variations in the depth of immersion of the thermometer
(5) variations in the size of the test flame
(6) variations in the rate of stirring.

The dimensions of the Pensky-Martens flash point apparatus are:

	Min. in.	Normal in.	Max. in.	Min. cm.	Normal cm.	Max. cm.
Inside diameter below filling mark . .	1·950	2·000	2·050	4·953	5·080	5·207
Difference inside and outside diameters below filling mark . .	0·120	0·125	0·130	0·305	0·318	0·330
Inside height . .	2·150	2·200	2·250	5·461	5·588	5·715
Thickness of bottom .	0·070	0·095	0·120	0·178	0·241	0·305
Distance from rim to filling mark . .	0·845	0·860	0·875	2·146	2·184	2·223
Distance lower surface flange to bottom of cup.	1·780	1·795	1·810	4·521	4·559	4·597

The oil to be examined is placed in the copper cup in such quantity as just to touch the mark which will be found on the inside of the cup. The volume of oil required is approximately 75 ml.



A. Oil Cup
B. Heating Vessel
C. Stirrer
D. Thermometer
E. Ignition Burner
F. Pilot Burner
G. Spring Handle
H. Revolving Shutter
J. Orifice

Fig. 12.—Pensky-Martens Apparatus.

Care should be taken to prevent wetting the cup above the mark. The cover with the thermometer fixed in position is then placed on the cup, and the injector burner lighted. The small flame should be 0·16 inch (3·9 mm.) in diameter.

The apparatus is heated by a Bunsen burner, or by electricity, at a rate of 9° to 11° F. per minute. The oil is stirred rhythmically at a speed of approximately one revolution per second. Too slow stirring does not ensure even temperature distribution, and too rapid stirring causes splashing. The first injection of the small flame is made 30° F. below the flash point, and then after every 5° rise, or every half-minute, until a distinct flash is seen within the cup. The time for lowering the flame into the cup should be 0·5 second and kept in position for 1 second, then it is withdrawn rapidly. Flash point should be recorded in multiples of 5.

The vapour from some oils extinguishes the ignition flame up to a temperature within a few degrees of the flash point. As the temperature of the oil increases vapour is evolved, but in insufficient quantity to carburate the air in the cup to the flashing point; its presence is, however, often detected by the sudden elongation of the ignition flame when it is injected. The flash takes place when the atmosphere inside the cup contains approximately 2 per cent of oil vapour by volume.

Oils containing minute quantities of volatile organic substances are liable to exhibit an irregular flash or flashes at a temperature below the true flash point of the oil. Such a flash is termed a "freaky" flash because, although a small flash is observed, the intensity of the flash does not increase with increased temperature. If the ignition flame is extinguished, as it sometimes is, freaky flashes occur, not necessarily from the oil, but through the ignition of the coal gas which has been injected into the apparatus from the ignition burner.

The presence of water in an oil may have considerable influence upon the flash point, either by lowering or raising it. The lowering of the flash point is probably due to the steam distillation of the lower members of the oil, whereas the raising is accounted for by the steam in the oil cup preventing the oil vapour from igniting. The advisability of removing water from the oil prior to determining the flash point is debatable. Fortunately the question does not often arise with unused oils, and perhaps fortunately the question is often settled for us with wet oils, as they spit and splutter when heated and make the determination impossible. Clearly, water which can be readily separated by decantation should be removed. If there is sufficient water present to affect the determination seriously it may be assumed that the oil is not ideal for lubrication. As used oils may contain water it may be considered prudent to remove the water, but care must be taken not to remove any volatile matter other than the water.

Free water may be removed by settlement, or centrifugal action.

Suspended water can be absorbed by the usual desiccants such as anhydrous calcium chloride, or by filtering through filter paper containing plaster of Paris. Oils which will not suffer loss of the more volatile portions may be dried by heating to 100° C. and passing a gentle current of air through it.

After every determination the apparatus should be dismantled and very carefully freed from oil, not forgetting the underside of the shutter on the cover. Flash point determinations are best performed in a room where the light is subdued.

Flash point (*open*) can conveniently be determined upon the oil which has been used for the closed flash point by removing the cover and placing on the cup an attachment carrying a thermometer and a fixed gas-jet. In this test the ignition flame is stationary. The rate of heating is as in the previous test.

In the U.S.A. the Cleveland open cup has been standardised. The ignition flame is passed over the surface of the oil, at successive 5° F. rise, in the plane of the upper edge of the cup.

Both of these methods give results sufficiently near to each other to render them interchangeable, but there are exceptions.

Some controversy exists over the relative merits of the closed and open flash points. The argument is not terribly important so long as one recognises that the closed test detects minute quantities of low flashing material which may or may not be important. There is much to be said in favour of the open flash point where trivial contamination is of no consequence.

Fire point is that temperature at which an oil just commences to burn continuously. In performing this test the thermometer must be watched carefully, because as soon as the oil begins to burn freely the temperature rises rapidly. The determination is just a continuation of the open flash point test. The fire point of an oil is approximately 60° F. above the open flash point.

The flash point of an oil furnishes no criterion whatever of its lubricating value. The tendency nowadays is to specify a figure in specifications merely as a safeguard. Specifications have often been issued in which the aim has been to put the flash point as high as possible, even to the point of irksomeness. There are some very false ideas current about the values of flash point, but they are gradually being eliminated. Do not go to the other extremity of ignoring entirely this test which is of value when considering fire risks.

Spontaneous ignition temperature is that temperature at which an oil will ignite when heated without the application of a flame. It must not be confused with flash point. In the U.S.A. it is described as the autogeneous ignition temperature. The method in use is to drop oil into a conical flask, about 11·4 cm. high, 6 cm. in diameter at the bottom, and 2·85 cm. in diameter at the top, which is heated in a solder bath. The temperature of the bath is indicated by a pyrometer. Various amounts of the sample are delivered from a pipette to the flask until ignition occurs. It is better to raise the temperature above the ignition temperature, and to work downwards from a higher temperature at first by intervals of from 5° to 20° C. by approximately 5° intervals. After each test all the gasses and vapours must be displaced by a current of air. If ignition takes place when one of the charges is added the temperature is lowered and the process repeated starting with the number of drops that ignited in the first instance. A larger and smaller number of drops should also be tried in order to be sure that the value of the test sample giving the lowest temperature of ignition shall be included in the tests.

The test is very much a matter of trial to get the approximate value, and then to make successive trials varying the temperature and volume until the lowest indicated ignition temperature is found.

Iodine value. Hübl's method is to allow a solution of iodine and mercuric chloride in alcohol to act upon the oil for a number of hours in the dark.

The iodine solution is prepared by dissolving 25 gm. of pure iodine in 500 ml. of 95 per cent alcohol, and the mercuric solution by dissolving 30 gm. of mercuric chloride in 500 ml. of 95 per cent alcohol. The mercuric chloride solution frequently requires filtering. The two solutions are kept separately until they are required for use, then equal volumes are mixed and allowed to stand for 24 hours before use.

The strength of the iodine solution so mixed is ascertained by titrating it with sodium thiosulphate solution, made by dissolving about 24 gm. of sodium thiosulphate crystals in 1,000 ml. of distilled water.

The sodium thiosulphate solution is standardised by weighing exactly 3·8657 gm. of pure potassium bichromate, dissolving it in distilled water, and making the solution up to 1,000 ml.; one ml. of the bichromate solution will liberate exactly 0·01 gm. of iodine. Approximately 10 ml. of a 10 per cent solution of potassium iodide in water are poured into a 500 ml. glass stoppered bottle, together with 5 ml. of strong hydrochloric acid; then exactly 20 ml. of the bichromate solution added when 0·2 gm. of iodine are liberated according to the following equation:

$$K_2Cr_2O_7 + HCl + 6KI = Cr_2Cl_2 + 8KCl + 7H_2O + 3I_2$$

The solution is allowed to stand for a few minutes after well shaking, then 300–400 ml. of distilled water are added, and well mixed with the contents in the bottle. The dark yellow colour is gradually discharged when the thiosulphate solution is slowly added from a burette. When the colour has become faint add a few drops of freshly made starch solution to produce the blue "starch iodide." Then continue to add the thiosulphate solution until the blue colour completely disappears on shaking. The volume of thiosulphate solution added is noted. From this the strength of the thiosulphate solution in terms of iodine is calculated.

Volume of bichromate solution used . . .	20 ml.
1 ml. $K_2Cr_2O_7$ solution liberates . . .	0·01 gm. iodide
20 ml. ,, ,, ,, . . .	0·2 ,, ,,
Volume of thiosulphate solution added . .	17·6 ml.
Hence 17·6 ml. $Na_2S_2O_3$ solution oxidise . .	0·2 gm. iodide
1 ml. ,, ,, ,, . .	0·01136 ,,

The iodine value of an oil is that weight of iodine which is absorbed by 100 gm. of oil.

It is determined by taking an accurately weighed quantity (0·2 gm. of a drying oil, 0·3 gm. of a semi-drying oil, 0·4 gm. of a non-drying oil, 1 gm. of a solid fat or mineral oil), and dissolving it in 10 ml. of a suitable solvent, e.g. chloroform, carbon tetrachloride, glacial acetic acid, etc., but not ether, contained in a 500 ml. stoppered bottle. Add exactly 25 ml. of the alcoholic iodine-mercuric chloride solution, shake, and allow to stand in the dark overnight, after replacing the stopper and moistening it with potassium iodide solution to absorb any iodine which might volatilise. A control test is made simultaneously by proceeding as above except that no oil is used.

At the expiration of about 18 hours, 20 ml. of 10 per cent potassium iodide solution in distilled water are added to each bottle, the first few drops being used to wash the stopper, and after a thorough agitation to dissolve the excess of iodine 300–400 ml. of water are added, and titrated with the standardised sodium thiosulphate solution as described above. From the differences between the number of millilitres required for the control and the test can be calculated the amount of iodine which has been absorbed by the oil.

Weight of oil	1·0536 gm.
Volume of iodine solution . . .	25 ml.
Volume of $Na_2S_2O_3$ required for control .	39·4 ml.
Volume of $Na_2S_2O_3$ required for test .	26·4 ml.
Difference	13 ml.
1 ml. $Na_2S_2O_3$ =	0·0119 gm. iodine
13 ml. $Na_2S_2O_3$ =	0·1547 gm. iodine
1·0536 gm. of oil absorbed	0·1547 gm. iodine
100 gm. of oil absorbed	14·67 gm. iodine
Iodine value	14·67 gm. iodine

Wijs' method is a modification of Hübl's method, and is preferred by some chemists because of the greater stability of the solutions used, and the shorter time required for complete absorption of the iodine by the oil.

IODINE VALUES

Class	Oil	Value
Vegetable:		
Semi-drying	Cottonseed	108–110
„	Rape	94–102
„	Rape blown	60–90
„	Ravison	101–122
„	Sesame	103–108
Non-drying	Groundnut	83–100
„	Olive	79–88
„	Castor	83–90
„	Coconut	8–10
Marine	Cod	154–181
„	Seal	127–193
„	Sperm	81–90
„	Whale	121–146
Animal	Neatsfoot	69–76
„	Lard	46–70
„	Beef tallow	38–46
„	Mutton tallow	35–46
„	Wool wax	17–28

Nine gm. of iodine trichloride are dissolved in 1,000 ml. of glacial acetic acid or in a mixture of 700 ml. of acetic acid and 300 ml. carbon tetrachloride, and the concentration determined, after which 10 gm. of powdered iodine are added, and shaken until the halogen is present to 1½ times the previous proportion. After filtering the liquid is diluted with acid until 5 ml. are exactly equivalent to 10 ml. of 0·1 N sodium thisulphate. The iodine is determined by adding

5 ml. of 10 per cent potassium iodide and 30 ml. of water to 5 ml. of the liquid and titrating with 0·1 N sodium thiosulphate solution. The glacial acetic acid and the carbon tetrachloride should be quite free from oxidisable matter.

The oil is dissolved in about 5 ml. of carbon tetrachloride, 25 ml. of Wijs' solution added, and after mixing left out of direct sunlight for 1 hour in the case of non-drying oils and 2 hours in the case of drying oils; 10 ml. of 10 per cent potassium iodide solution and 10 ml. of water are then added and the solution titrated with 0·1 N thiosulphate solution. A blank test is made simultaneously.

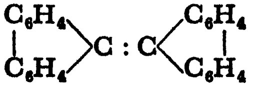
The procedure is then exactly the same as with Hübl's method.

Solvents which reduce potassium bichromate and strong sulphuric acid should be rejected.

A comparison of the two methods on mineral oil and the influence of time is shown in the table.

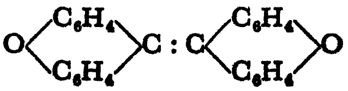
Hours	Hübl	Wijs
2	10·7	23·7
4	10·7	25·6
8	11·6	29·9
18	12·9	31·7
48	13·2	32·4

From these results it is evident that the absorption of iodine when determined under these conditions is somewhat irregular, and cannot be relied upon to measure the degree of unsaturation of the hydrocarbons in the mineral oil. Mineral oils differ in constitution from fatty oils, therefore it does not follow that because the degree of unsaturation can be measured in fatty oils that the same method will give equally satisfactory results with mineral oils. The power of an unsaturated group to unite with bromine depends upon the influence of its adjacent groups in the compound. Tetraphenylethylene, $(C_6H_5)_2C:C(C_6H_5)_2$ is unsaturated, yet it does not combine with bromine, whereas diphenylethylene $(C_6H_5)_2C:CH_2$ does. The closely allied compound tetraphenylene-ethylene



$$\begin{array}{c}\mathrm{C_6H_4}\\ | \\ \mathrm{C_6H_4}\end{array}\!\!>\mathrm{C}:\mathrm{C}<\!\!\begin{array}{c}\mathrm{C_6H_4}\\ | \\ \mathrm{C_6H_4}\end{array}$$

does combine with bromine, but its oxide only combines with difficulty



$$\mathrm{O}<\!\!\begin{array}{c}\mathrm{C_6H_4}\\ \mathrm{C_6H_4}\end{array}\!\!>\mathrm{C}:\mathrm{C}<\!\!\begin{array}{c}\mathrm{C_6H_4}\\ \mathrm{C_6H_4}\end{array}\!\!>\mathrm{O}$$

These examples of steric hindrance serve to illustrate that iodine absorptions are of limited value unless the constitution of the compounds under test are known. Since mineral oils are complex mixtures of complex compounds of very uncertain constitution, it is not surprising that difficulties should be encountered.

Hübl and Wijs' Methods Compared

Oil	Sp. Gr.	Hübl	Wijs
American:			
Cylinder . . .	0·875	10·2	22·8
Engine . . .	0·901	9·9	30·5
Spindle . . .	0·901	10·8	34·0
Cylinder (black) . .	0·900	13·9	30·9
Russian:			
Cylinder . . .	0·914	9·9	22·0
Engine . . .	0·904	6·4	16·8
Spindle . . .	0·899	4·5	14·4
Scotch:			
A	0·873	31·6	56·8
B	0·890	24·5	49·8
C	0·902	19·5	43·6

It has often been assumed that mineral oils of high iodine value necesssarily have high oxidation values. Waters found that of several oils oxidised, one having the highest iodine value showed the least oxidation.

Loss on Heating of transformer and switch oils. Michie's toluene-vapour bath method was adopted many years ago by the British Electrical and Allied Industries Research Association, and later accepted as a standard method by the Institute of Petroleum. The apparatus consists of a metal bath fitted with a reflux condenser. The upper portion of the bath contains a trough, the ends of which are closed by removable end-pieces. The oils to be tested are weighed into flat-bottomed, straight-sided, cylindrical glass beakers 38 mm. internal diameter and 38 mm. internal depth, weighing between 10 and 15 gm. For comparative purposes it is considered preferable to use a constant volume of oil to a constant weight, therefore exactly 20 ml. of oil is put into the beaker, which is afterwards weighed. The beakers are placed in the trough and surrounded to within one-eighth of an inch of the top of the beakers with lead shot, 0·064 inch diameter. By boiling toluene in the bath a uniform temperature of 100° C. is maintained in the oil. Until experience has been gained with the method it is wise to insert a thermometer into the lead shot to check the temperature. Violent boiling of the toluene may create congestion in the condenser and an overflow, and a fire; on the other hand excessive caution may lead to insufficient heating of the beakers. When lighting up, the bath must be watched to avoid a fire. The heating is continued for 5 hours, after which the beakers are removed, cooled and weighed.

The evaporation loss is varied by air currents across the beakers; consequently, to avoid these variations a screen 6 inches deep by 12 inches by 7 inches is placed on the bath to surround the beakers. The loss is also varied by the time of heating, therefore the beakers are placed in position when the toluene is boiling. Admittedly, the oil takes time to reach 100° C., but no allowance is made, it is simply included in the 5 hours.

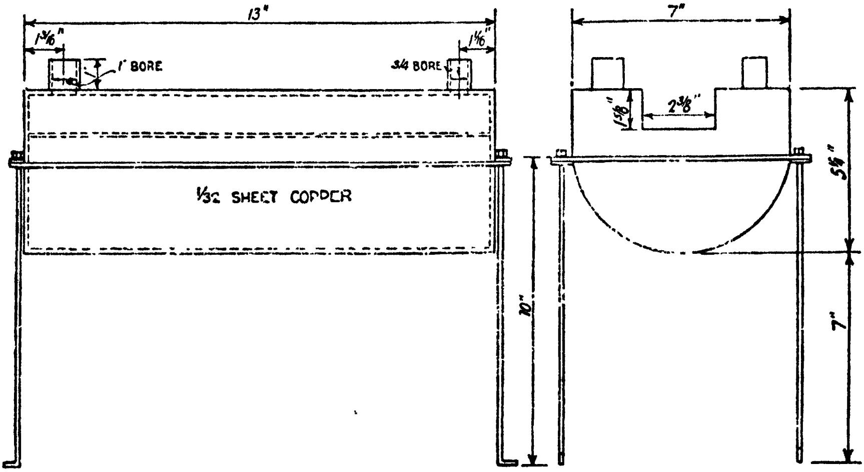


Fig. 13.—Toluene Vapour Bath.

The result is expressed as the loss per cent by weight.

This method is not serviceable to oils with a viscosity much higher than that of transformer oils simply because the loss is so small. Should evaporation loss figures be required it is better to use petri dishes of equal size and heat them in an oven which has a uniform temperature. It is not very often that evaporation tests are required. When they are done repeat tests should be made as they are not extremely reliable.

Oxidation Test for lubricating oil looked particularly hopeful when it was established that most solid deposits in engines are oxidation products. Time and experience has, however, revealed that a simple oxidation test cannot classify all oils into their sludge-forming groups. Even suggested modifications of the test have failed to generalise, but for specific purposes the test is useful, and perhaps valuable. The British Air Ministry has introduced an oxidation test combined with the Ramsbottom Carbon residue test into its specification for aero engine lubricating oil. How far the test can be applied to petrol engine oils in general is yet to be determined.

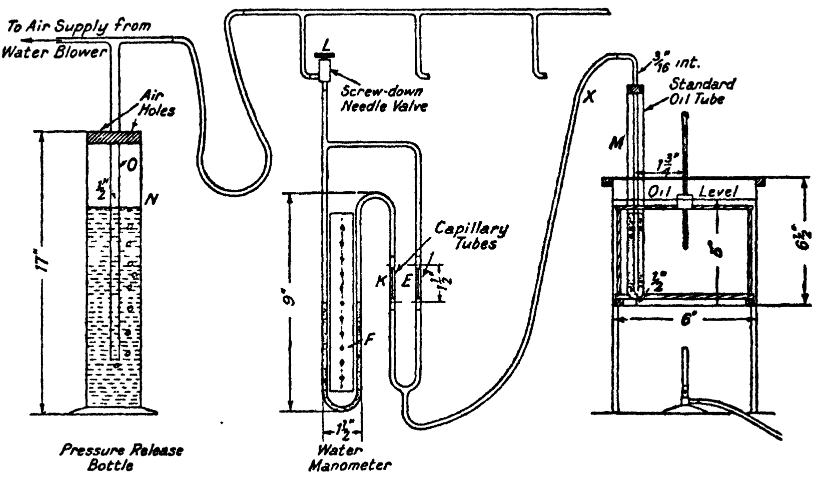


Fig. 14.—Air Ministry Oxidation Test.

Into a boiling tube, 250 mm. by 25–26 mm. is placed 40 ml. of oil. The tube is supported in an oil-bath which is maintained at a temperature of 200 ± 0·1° C. Air is passed through an inlet tube, 4·6–5·0 mm. internal diameter, into the oil, emerging as near to the bottom of the boiling tube as possible.

To obtain consistent results regard must be paid to detail. Careful attention must be given to temperature regulation whether the heating be done by gas or electricity. When gas heating is employed the metal oil bath can be shielded with a metal surround up which the hot gases can pass. Electrical heating follows the usual course with ample lagging. A small oil bath is not satisfactory. It is much better to use one containing about 3 gallons of oil. Any high flash point oil may be used, but a good filtered cylinder oil of low pour point is best. Of course the oil must be well stirred.

Air from an adequate size blower is passed, via a cotton wool or glass wool filter, into a pressure stabiliser, by a tube, not less than 12·5 mm. internal diameter, thence by way of a screw-down needle valve or other sensitive control and a capillary tube to the air inlet tube. The stabiliser is a tall cylinder containing water to a depth sufficient to provide the requisite air pressure. There must always be an excess of air escaping from the tube. Too rapid an escape is bad as it disturbs the water level and encourages evaporation. It is assumed that the air in the laboratory is reasonably pure. The object of the needle valve is to control the flow of air to the capillary tube. A capillary tube makes an excellent part of an air-flow meter. It restricts the air flow, and so builds up a pressure on the inlet side, and gives a depression on the outlet side. When these two sides are connected to a differential manometer it is only necessary to watch the differences in level to ensure steady flow. But it is first necessary to adjust the air through-put to 15 ± 0·25 litres per hour by suitable attention to the stabiliser, needle valve and choice of capillary.

The boiling tubes are carried in a cradle in the oil bath, so fixed that the tubes emerge 76 mm. above the lid of the bath. The exposed portion of the tube should be protected against draught by a shield 152 mm. high, and the oil in the bath should be 12·5 mm. from the lid when hot. After a test has been made the tubes should be thoroughly cleaned with concentrated sulphuric acid to remove any stain or residue, finally washed with water and dried. This also applies to the air inlet tube. Corks can be washed with hot solvent, but they are not suitable after several tests.

The test is made in two parts to avoid the necessity of having to arrange for a long period of supervision. The actual blowing time is 12 hours, but this is divided into two periods of 6 hours each. At the end of the first 6 hours the boiling tubes are removed from the oil bath and allowed to stand at atmospheric temperature for 12–18 hours. The next morning the oil bath is reheated and the tubes reimmersed and blowing continued for the second 6 hours. At the end of the blowing period the tubes are withdrawn, allowed to cool, and to stand 15–30 hours. After this rest period the Ramsbottom carbon residue and the viscosity are determined on the blown oil, but before the requisite quantity is withdrawn the boiling tube is heated in a boiling water bath for 20 minutes and well shaken to ensure that any precipitate is evenly dispersed.

The kinematic viscosity is determined at 100° F. in one of the U-tube capillary viscometers described under the heading "viscosity." The viscosity ratio $\frac{\text{viscosity after oxidation}}{\text{viscosity before oxidation}}$ is calculated. Sometimes it is called blowing ratio or simply B.R.

The Ramsbottom carbon residue is determined before and after blowing. Sometimes the carbon residue before blowing is spoken of as coke (*a*), and after blowing as coke (*b*).

Discussion has taken place upon the advisability of varying the weight of oil used for the carbon residue test after blowing, in fact in Standard Methods a recommendation is made. Probably it is wise to regard this as a tentative recommendation until more considered views have been expressed. The idea is new and may require a greater accumulation of data.

The oxidation test should always be made in duplicate, and if time permits, repeated, as unaccountable freak results do occasionally appear.

Power factor of cable oils may be defined as the ratio of the actual work done to the apparent work done. Low power factor can be likened to a man doing a certain amount of work with a lot of useless but apparent energy, whereas high power factor is like a man doing a job with the minimum effort. Power factor is obtained by dividing actual work by apparent work. Although power factor cannot be greater than unity it is usually expressed in parts per hundred. It is desirable to have the power factor as high as possible.

In an electric circuit consisting of a single pair of wires operating on alternating current the voltage may be designated as E, the amperes as I, and the watts by W. Then

$$W = EIK$$

$$K = \frac{W}{EI}$$

The power factor K is

$$K = \frac{W}{EI} 100$$

W represents the actual work and the product EI the apparent work.

That a high power factor is desirable is clear from the fact that if the voltage, E, remains constant the number of amperes, I, that will be transmitted through the circuit will be greater as the power factor, K, increases.

For electrical insulations, however, the power factor should be low. When the two plates are separated by a sheet of insulating material and a current applied, a feeble current flows through the insulation, and manifests itself as heat. This feeble current cannot be employed usefully, and is described as dielectric loss. Any loss of current should be avoided as much as possible.

The formula given above holds for insulations. Hence the way to reduce the loss is by lowering the power factor.

Resistivity test for cable oils is generally stated in terms of ohm-cm. or megohm-cm. at a designated temperature. This unit implies that the resistivity is the amount of resistance offered by an oil to the flow of current through it when it is subjected to a direct current voltage. The oil is considered to be in the form of a cube and resistivity is the electrical resistance between two opposite faces of the cube. Because of the magnitude of this value it is obvious that the oil has to be measured in a state approaching a film. The measurements are made by means of a cell which contains an upper electrode and a lower electrode. In the cell generally used in America the upper electrode has an area of approximately 56 square centimetres. The lower electrode is somewhat larger and is made in the form of a bowl to contain the oil. The electrodes are placed 0·5–1·0 mm. apart. A guard ring is usually provided for the upper electrode.

It will be seen that the sample of oil consists of a layer of oil not more than 1 mm. thick and an area of 56 square centimetres. Across this area of oil is impressed a direct current of 100–200 volts. A galvanometer with shunt is connected in series with the oil and the electrical supply. The oil is heated to any designated temperature, the American practice being usually about 80° C.

From the known galvanometer constant and its deflection may be calculated the number of ohms or megohms offered by the oil film. If M represents the megohms then the megohm-cm. resistivity can be calculated from the formula

$$r = \frac{A}{D} M$$

where A is the area of the upper electrode, D the thickness of the oil between the electrodes, and r is the resistivity.

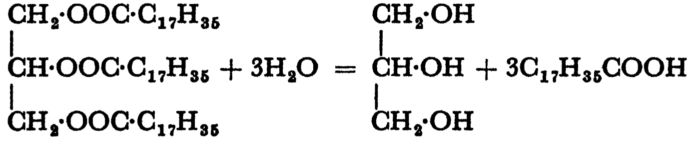
A cable oil should have a high resistivity.

Cable oils which have a high resistivity will produce cables of very low power factor. This is a very desirable property.

In order to determine whether the oil will retain its resistivity when it is heated in the presence of air, about 3 cm. depth of oil is heated in a 400 ml. beaker at 100° C. The resistivity is measured periodically for 10 days. The oil should sustain its resistivity.

Saponifiable Matter. The saponification value of an oil is the number of milligrams of potassium hydroxide required to saponify one gram of oil. In the past it has been common practice to give the saponification value of an oil. Many specifications still demand it, and it is sometimes determined in used oils. To determine the amount of saponifiable matter in an oil the saponification value is usually measured. It is the basis of the volumetric determination of saponifiable matter. When the problem is simply the estimation of fatty oil in mineral oil it is comparatively easy to state the percentage of saponifiable matter present, but the growing use of chemical addition agents complicates the issue considerably. An entirely new technique may be necessary to cope with the new order of things. For the immediate future saponifiable matter should be regarded as fatty matter with the knowledge that it may be other compounds.

The saponification or hydrolysis of a fatty oil or wax is the process of decomposing it into fatty acids and alcohols with a hydrolysing agent. The terms saponification and hydrolysis are not quite synonymous although they are often interchangeable. Saponification, as the word indicates, essentially involves the formation of soap, so that when a fat is split into fatty acids and glycerol by an agent which is capable of combining with the fatty acids, such as potassium hydroxide, to form soaps, saponification is said to have been effected. If, however, the agent is not capable of combining with the acids to form soaps, then only hydrolysis has taken place. Suppose the agent be steam, or an acid, no saponification results but hydrolysis. The saponifying or hydrolysing substance is a medium for the addition of water to the fat constituents.



$$\begin{array}{lcl} CH_2\cdot OOC\cdot C_{17}H_{35} & & CH_2\cdot OH \\ | & & | \\ CH\cdot OOC\cdot C_{17}H_{35} + 3H_2O & = & CH\cdot OH + 3C_{17}H_{35}COOH \\ | & & | \\ CH_2\cdot OOC\cdot C_{17}H_{35} & & CH_2\cdot OH \end{array}$$

A saponifiable solution must become gradually weaker as the saponification proceeds, because it is being converted into soaps, whereas theoretically an acid agent can hydrolyse an infinite amount of fat. This is important in lubrication.

The saponification value of an oil serves as a useful means of identifying it. True, it is not a fixed value, but it only varies within narrow limits, sufficiently narrow to be of service. Unfortunately more than one fatty oil may have approximately the same saponification value, hence this value can only be used in conjunction with other data in the analysis of an oil.

SAPONIFICATION VALUES OF OILS FOUND IN LUBRICANTS

Class	Oil	Value
Vegetable:		
Semi-drying	Cottonseed	193–195
	,, stearine	195
	,, blown	220–260
	Rape	170–179
	,, blown	220–260
	Ravison	174–179
	Sesame	189–193
Non-drying	Groundnut	190–196
	Olive	185–196
	Castor	183–186
	Coconut	246–260
Marine . .	Cod	171–189
	Seal	189–196
	Sperm	123–147
	Whale	188–194
Animal . .	Neatsfoot	194–199
	Lard	195
	Beef tallow	193–200
	Mutton tallow	192–195
	Wool wax	102

It will be observed from the values of sperm oil and wool wax (Yorkshire grease) that they are much lower than that of other oils. The reason for this is that these two fatty materials are waxes and not oils. There is a profound difference between an oil and a wax. It is an oil is a combination of fatty acids and a trihydric alcohol whereas a wax is a combination of fatty acids and a monohydric alcohol. The trihydric alcohol is always glycerol, but the monohydric alcohol is not confined to one representative member.

About 1·5 grams of a fatty oil or an equivalent amount of a compounded oil, are weighed accurately in a round-bottomed flask of about 200 ml. capacity, then 25 ml. of an approximately seminormal solution of potassium hydroxide in alcohol are added. This solution is made by dissolving the requisite amount of potassium hydroxide, which shall be as free from carbonate as possible, in the minimum quantity of carbon dioxide free distilled water, and then diluting the resultant solution with absolute alcohol. In view of the enormous excise duty on absolute alcohol there is a temptation to use weaker and less pure alcohol. Under certain circumstances it is possible to obtain an industrial methylated spirit duty free which is good enough for this purpose. When using a 95 per cent alcohol the potassium hydroxide should be dissolved in sufficient of it and the remainder added after the solution has been effected.

A long tube of not less than ¼-inch bore and about 3 feet long is fitted to the flask to serve as a condenser. The flask is placed on a water bath containing boiling water, or an electrically heated hot-plate, and boiled. The time required for complete saponification varies with different oils, but generally half to one hour is sufficient for fatty oils, provided ebullition is fairly vigorous. For compounded oils it may be anything up to 3 hours, therefore 3 hours boiling is now generally adopted. Simultaneously a similar flask containing 25 ml. of the alcoholic potash solution is heated for the same period. This control experiment is done so that if the alcoholic potash should alter in strength during the heating through absorption of carbon dioxide, and dissolving the constituents of the glass, etc., a correction can be applied. Then the two flasks are cooled, a few drops of an alcoholic solution of phenolphthalein added to serve as an indicator, and the two solutions titrated separately with semi-normal hydrochloric acid. Hydrochloric acid is better than sulphuric acid on account of its salt being soluble.

EXAMPLE

Weight of oil 1·2392 grams
Control 25 ml. KOH solution requires 22·7 ml. $\frac{N}{2}$ HCl
After saponification 25 ml. KOH requires 14·9 ml. $\frac{N}{2}$ HCl
Since 1 ml. $\frac{N}{2}$ HCl $= \frac{0{\cdot}0561}{2}$ gram KOH
Then $\frac{(22{\cdot}7-14{\cdot}9)\times 0{\cdot}0561}{2} = 0{\cdot}2184$ gram KOH
were required to saponify the oil
i.e. 1·2391 gram of oil required 0·2184 gram KOH
or 1·2392 ,, ,, 218·6 mgm. KOH
1 gram of oil would require $\frac{218{\cdot}4}{1{\cdot}2392}$ mgm. KOH
= 176 mgm. KOH
Hence saponification value = 176

Determination of Fatty Oil in a Compounded Oil. The saponification value of the oil is first determined, then by a simple calculation the amount of fatty oil can be estimated approximately, thus

$$\frac{\text{Saponification value per cent} \times 100}{\text{Saponification value per cent of fatty oil}} = x \text{ per cent of fatty oil.}$$

When the saponification value of the fatty oil is unknown assume a saponification value per cent of 20 as being approximately the mean saponification value per cent of the common fatty oils. Of course, by this method the result can only be approximate, but it is often sufficiently near for practical purposes.

To diminish the time required for saponification a variety of higher boiling-point solvents have been tried, but the results have not been successful. The introduction of methyl ethyl ketone and carbitol have placed at our command two solvents which are showing great promise. At the moment they are being added to the ethyl alcohol.

Determination of Mineral Oil in a Compounded Oil. A weighed quantity of oil containing not more than 1·5 gm. of fatty oil is saponified in the usual way, the excess of potassium hydroxide is neutralised with dilute sulphuric acid, and then remade slightly alkaline with potassium hydroxide. Petroleum ether, B.P. 60/80° C., is added to the flask to dissolve the unsaponified oil. The author prefers petroleum ether, B.P. under 40° C., because it is more easily evaporated, and less prone to emulsify. Then the contents of the flask are very carefully transferred to a separating funnel. In order to ensure the complete transference of the contents of the flask into the funnel the flask should be washed out three times at least with small quantities of petroleum spirit, then several times with water and finally with petroleum spirit. The whole of the washings must be added to the main bulk in the funnel. This done, the funnel is stoppered, and shaken for a few minutes with an alternating circular motion. Should the shaking be done too vigorously the two solutions are liable to form an emulsion which may be difficult to disperse. On standing undisturbed the solutions will separate into two distinct layers, the upper layer being the petroleum solution of the unsaponifiable matter and the lower layer the aqueous solution of the soap, etc. The lower layer is run off.

Where considerable accuracy is of importance the aqueous solution should be shaken with more petroleum spirit, separated, and the ethereal solution added to the other separating funnel. In works' laboratories this is frequently omitted.

The ethereal solution is washed several times with warm distilled water, shaking and allowing to separate as before after each washing. Emulsions sometimes occur, but after a little practice one can usually avoid them. When they occur there are various methods by which they can be eliminated, but, of course, prevention is better than cure. A light emulsion may be broken by shaking with a wire in the mixture, or by warming on a water bath. Sometimes the addition of a little alcoholic potash is effective. Should these methods fail, collect the emulsion in another funnel, shake violently, and extract with a large volume of petroleum spirit. The presence of a little alcohol often assists in the resolution. What might appear to be a stable emulsion on the first washing may rapidly disperse after a few washings. The washings should always be continued until the wash water is perfectly neutral. Then carefully drain off the last traces of water, and allow the ethereal solution just to fill the drilled portion of the tap. This being done, dry the stem of the funnel with filter paper, and run the solution through about 1 gram of plaster of Paris contained in a small filter, to remove any water which may be dissolved in the spirit. The solution is collected in a weighed small flask. Wash the funnel several times with petroleum spirit, each portion is passed through the filter, care being taken to see that the whole of the interior of the funnel and the edges of the filter are washed. The petroleum spirit is distilled off nearly to dryness on a water bath, and the residue dried in a water oven and weighed. The drying in the oven should not be prolonged more than is essential, because all mineral oils are more or less volatile even at 100° C. No residue should require more than 2 hours' heating.

Difficulties will arise when one is dealing with burning oils or other hydrocarbons of low boiling-point.

Determination of a Fatty Oil in a Compounded Oil by estimating the Glycerol Content. Five to ten grams of the compounded oil, according to the amount of fatty oil present, are saponified with an excess of alcoholic potash, the actual amount being immaterial. Boil for about 3 hours under a reflux condenser, then remove the condenser, and boil off the alcohol. When all the alcohol has evaporated re-dissolve in boiling water, and acidify with dilute sulphuric acid to liberate the fatty acids. This solution is very prone to bump, hence it is advisable to add a small piece of glass rod to ensure steady ebullition. Boil until the aqueous solution is perfectly transparent, then filter as rapidly as possible, taking care to keep the filter full the whole time, and so avoid the risk of the oil and fatty acids passing through the paper; wash with boiling water until the washings are free from sulphuric acid. The filtrate containing the glycerol is concentrated, and the free sulphuric acid removed by the addition of an excess of barium carbonate. After the addition of the barium carbonate care must be taken to avoid spitting as the solution approaches dryness. The dry mass is extracted with alcohol-ether (1 : 1), the solution being passed through a filter into an acetylation flask. The alcohol-ether is distilled off on a water bath, and the impure glycerol is boiled with about 5 ml. of acetic anhydride and about 1 gram of anhydrous sodium acetate for approximately 2 hours.

An acetylation flask is simply a round-bottomed flask fitted with a ground-in glass air condenser.

Anhydrous sodium acetate is prepared by gently heating the crystalline salt until it just fuses without blackening.

Allow the acetylation product to cool, add carbon dioxide free water and warm, not boil; when solution is complete filter into a 1,500 ml. flask. The acetic acid in the filtrate is *exactly* neutralised with 2 per cent sodium hydroxide solution, then a known quantity of 10 per cent sodium hydroxide solution of known strength is added, and the solution is boiled gently under a reflux condenser for half an hour to hydrolyse the triacetin.

Triacetin being volatile in steam it is essential that complete condensation of the steam is effected. Cool and titrate the excess of sodium hydroxide.

Weight of oil 19·6000 gm.

25 ml. 10 per cent NaOH require 118·1 ml. $\frac{\text{HCl}}{2}$

After hydrolysis 113 ml. $\frac{\text{HCl}}{2}$ were required

$$118{\cdot}1 - 113 = 5{\cdot}1 \text{ ml.}$$

1 ml. $\frac{\text{HCl}}{2}$ corresponds to $\frac{0{\cdot}092}{3} \times \frac{1}{2}$ gm. of glycerol

$$\frac{5{\cdot}1 \times 0{\cdot}092 \times 1}{3 \times 2} = 0{\cdot}0782 \text{ gm. of glycerol}$$

Fatty oil contains 5 per cent (approx.) of glycerol

$$\frac{0{\cdot}0782 \times 100}{5} = 1{\cdot}56 \text{ gm. of fatty oil}$$

19·6000 gm of oil contain 1·56 gm. of fatty oil

100 gm. of oil contain $\frac{1{\cdot}56 \times 100}{19{\cdot}6} = 8$ per cent

Determination of a Fatty Oil in a Compounded Oil by the Fatty Acid Content. Sometimes it is convenient to estimate the fatty acids in a compounded oil, and then to calculate the amount of fatty oil present therefrom. As most fatty oils contain about 95 per cent of insoluble fatty acids it is not always necessary to know the nature of the fatty oil present. There are some exceptions, however, the most important being:

Dolphin-jaw	66·3
Palm nut	88 –91
Coconut	82 –90
Butter	85·5–90
Sperm	60 –64
Wool wax	59·8

A quantity of oil, containing about 1–2 gm. of fatty oil, is saponified, the excess of alcoholic potash nearly neutralised, the mineral oil extracted with petroleum spirit in the usual way, and the aqueous extract containing the soap and glycerol is evaporated to dryness to remove the alcohol. It is preferable to remove the alcohol after extracting with petroleum spirit rather than before. The dry soap is re-dissolved in water, and the solution boiled, and the fatty acids liberated by dilute sulphuric acid. When the fatty acids have separated completely they are transferred to a filter and washed continuously with hot water. The fatty acids are transferred to a weighed dish, washing the filter paper with ethyl ether. The acids are dried in a water oven and weighed.

Sludging Value of transformer oil has created considerable international interest, and much effort has been made to induce the various nationals to agree upon one test, but without success. Each country which has contributed to the many conferences feels that it has strong reasons for its own particular course of action. In this country the Michie sludge test, which was proposed in the *Journal of the Institution of Electrical Engineers* in 1913, has been standardised under the title of sludging value. The test is accepted for transformer oils, but it is also a useful oxidation test for lubricating oils.

100 gm. of oil are introduced into a round-bottomed flask, fitted to a water condenser by a ground joint, and blown with 0·07 cubic feet (approximately 2 litres) per hour for 45 hours at 150±0·5° C. in the presence of copper. At the end of the blowing period the flask is removed from the oil bath, cooled to below 50° C., the oil transferred to a beaker and diluted with 450 ml. of I.P. petroleum spirit. Any adhering sludge is removed from the flask with some of the petroleum spirit and mechanical means if necessary, and added to the beaker. After well mixing, the beaker is placed

in the dark for 16–24 hours to allow the sludge to separate. Filtration is conducted through a weighed, dry, good quality, filter paper. Sometimes the filtration is slow, so the liquid should be decanted through the filter paper before any of the sludge is transferred. Then the sludge is washed twice with about 75 ml. petroleum spirit, after which the sludge is also transferred to the filter, and washed free from oil. The volume of petroleum spirit used for the total washing should not exceed 450 ml. The filter paper containing the sludge is dried at 90–100° C. until constant in weight.

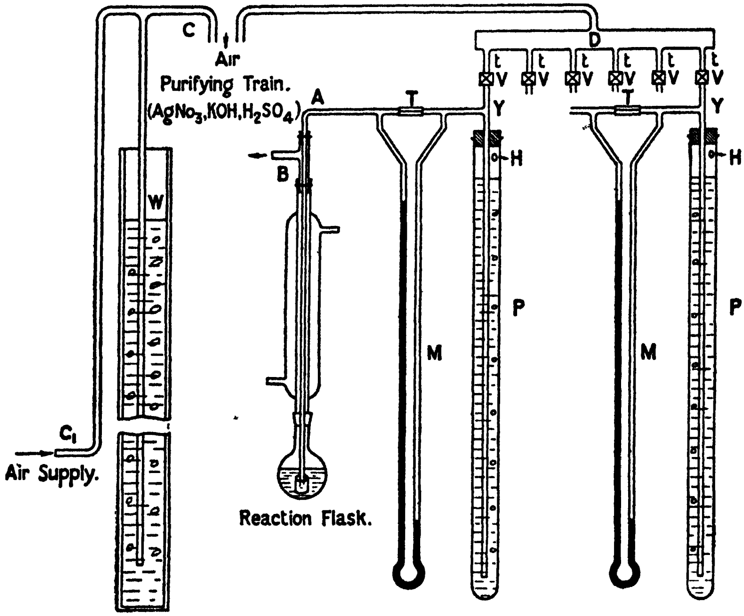


Fig. 15.—Sludging Valve Apparatus.

The result is reported as the percentage of sludge by weight. Different opinions exist upon the reproducibility of the test, and even the repeatability. The defenders claim that if all the details are observed good repeatability is possible, but they admit that curious results do creep in which may be ignored provided there is sufficient agreement between other results. Under these circumstances there seems to be little to be gained by reporting the result beyond the first decimal point if the value is above 0·1 or to the second decimal point when it is under 0·1.

The general assembly of the apparatus is shown in the diagram. When the tests are being made at regular intervals it is convenient to have a good copper circular bath large enough to hold six or seven flasks, even if all the spaces are not always occupied. The bottom frequently has to withstand superheating whilst the oil is heating up from cold, and this is intensified when sludge forms on the bottom; therefore it must be sufficiently thick to avoid burning out. Any high flash point mineral oil can be used. To avoid unnecessary fumes an effort should be made to obtain as high-class filtered cylinder oil as possible, not only for this oil bath but for any oil bath. One with a pour point of below 25°F. will be found advantageous, particularly when a stirrer must be started when the oil is being heated. When operating a bath at 150°C. the bottom must be brazed on to the side—solder should not be regarded as safe. There is no need to make the lid of copper, a good sheet iron is perfectly satisfactory. Holes are punched out of the lid symmetrically round the centre just large enough for the flasks to pass through. In the centre fit a boss to act as a bearing for a spindle carrying on the lower end a stirrer as large as possible. At the upper end a pulley is fitted to turn the stirrer. On the bottom of the bath a small footstep bearing is provided into which the spindle fits. In addition a small hole is drilled into the lid through which a thermometer can pass, also a slot for a thermo-regulator. Toluene cannot, of course, be used in the thermo-regulator, but a thin mineral oil can be used with safety. To keep the flasks off the bottom of the bath and to leave space for the stirrer paddle a cradle is provided on which the flasks rest.

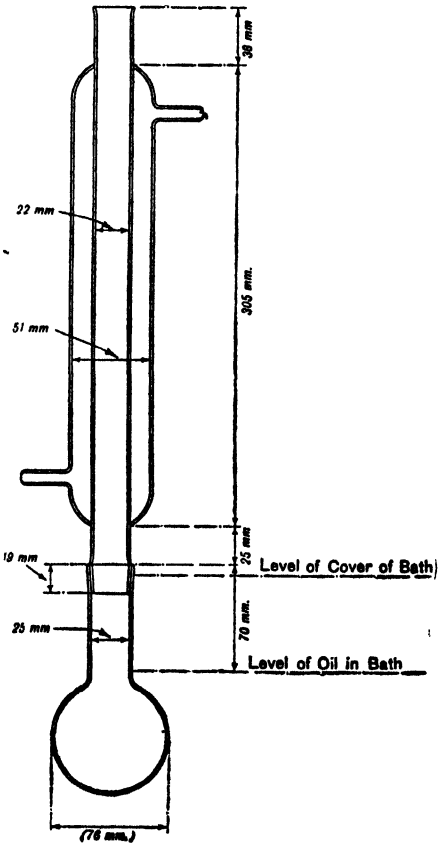


Fig. 16.—Reaction Flask.

It matters little how the air is forced through the flasks provided it is steady. This qualification limits one's scope considerably. Compressed air in cylinders is not continuously satisfactory due to the gradual diminution of pressure and therefore flow. Without doubt a mechanical air pump is to be recommended. A suction pump must not be used as it reduces the pressure in the flask and encourages evaporation of volatile constituents. Further reference to these constituents will be made. The first air-flow regulation occurs in a pressure compensator which consists of a column of water or thin oil (oil for preference) to give a hydrostatic head. The air then passes through a purifying train consisting of silver nitrate to remove hydrogen sulphide, potassium hydroxide to arrest acids, strong sulphuric acid to absorb water, and glass wool to catch any spray. Just how far these various wash bottles are necessary depends upon the condition of the air. In the oxidation test they are dispensed with; presumably it is assumed that the air is free from deleterious contaminants in a laboratory devoted to oil analysis. As they are specified in the standard method it is well to include them. To guard against the possibility of the reagents being forced over from one bottle into another when the air is shut off, a safety reservoir is inserted on the pressure side of each bottle. The air is led to a distributor, thence to the air-meter, which is similar to that used in the oxidation test. A capillary tube about 100 ml. long and having an internal bore of 0·3 mm. will be found convenient. By adherence to the recommended dimensions of the air-flow service a close approximation to the requisite air flow will result, but it is prudent to check it with a mechanical gas meter.

The constant pressure tubes, P, are approximately 760 mm. long and have an internal diameter of not less than 32 mm. An air escape hole, H, of about 13 mm. is made at the upper end of the tube. The tubes, Y, and the manometers, M, have an internal diameter of 6·4 mm. The air escape is adjusted by a valve, V, so that the individual bubbles are about 15 cm. apart. The difference in level in each manometer must be ascertained separately owing to slight variations in the dimensions of the capillary. The air supply to the wash bottles is adjusted to about 91 cm. (36 inches) by the pressure compensator W. To obtain the correct size of air bubble passing through the oil it is important that the air tube to the flask shall be 3 mm. ($\frac{1}{8}$ inch) internal diameter. (Fig. 15.)

The rate and type of oxidation can be varied by the presence of copper, and as bare copper may be present in a transformer it is reasonable to introduce copper into the sludging oil. A rectangular piece of electrolytic copper sheet 51 mm. (2 inches) by 32 mm. (1·25 inch) is polished on both sides by means of cotton wool and No. 150 carborundum powder, the powder being finally and thoroughly removed by successive wads of cotton wool. The copper is then rolled into a cylinder 32 mm. high with the edges just touching. After washing it with ether and drying it is put into the flask and the air inlet tube placed axially through it.

Usually the temperature of the water passing through a condenser is ignored, but in this test it must be observed, and regulated to between 15° and 20° C., by special means if necessary, and the rate of flow shall be such that the rise in temperature shall not be greater than 5° C. This is necessary to regulate the condensation of vapours which probably play an important part in the course of the oxidation reaction.

The I.P. petroleum spirit used must conform to the following specification:

Specific Gravity at 60°F./60°F.	0·680 — 0·680
Doctor Test	Negative
Colour	Water white
Distillation Test:	
Initial Boiling-point	55° C. (minimum)
Distilling between 60° and 80° C	90 per cent by volume
Final Boiling-point	90° C. (maximum)
Aromatic Content	Less than 0·5 per cent by weight
Bromine Value	Less than 1 per cent

A test which necessitates maintaining an oil bath at 150° C. for 45 consecutive hours raises the serious issue of fire hazard or guardianship at night. In the oxidation test this embarrassment is eliminated by making the test in two periods of 6 hours each. The author has introduced into his laboratory a modification of the sludging test not only to overcome this disadvantage but to speed up routine tests for works output. The modifications are: the temperature is increased to 200° C., the total air flow to 500 litres, and the time of blowing reduced to 7 hours. The two methods give almost identical results; in fact, the modifications were designed so that this should be so. The modified method is not a competitor to the original method but as a convenience to those who cannot adopt night work or delay laboratory reports.

Michie Sludge	Evans Oxidation	Sligh Test
Per cent	Per cent	Per cent
1·1	1·3	22·5
0·8	0·9	19·6
0·6	0·7	15·0
0·5	0·6	12·9
0·2	0·1	6·5
0·1	0·08	1·8
0·05	0·07	nil
0·03	trace	nil
nil	nil	nil

Sligh test results are given purely as a matter of interest. Details of the test are not given because the test has gone from favour. It survived in Sweden until 1939, but by now it has probably faded out there.

Specific Gravity of a substance is the ratio of the mass of any given volume of that substance at temperature t_1, to the mass of an equal volume of water at temperature t_2. The density is the mass of unit volume at $t°$. Specific Gravity should not be confused with density. The density only coincides with specific gravity when the units are chosen in a special way (cm. and gm., decimetres and kilograms, metres and metric tons). In the petroleum industry the specific gravity of an oil is expressed:

$$\text{Sp. Gr.}\ \frac{60°\ \text{F.}}{60°\ \text{F.}} = \frac{\text{Mass of a given volume of oil at } 60°\ \text{F.}}{\text{Mass of an equal volume of water at } 60°\ \text{F.}}$$

The temperatures t_1 and t_2 are each taken as 60°F. purely as a matter of convenience, and general consent.

In the U.S.A. the American Petroleum Institute has adopted what is called the A.P.I. gravity. It is purely an arbitrary figure, but it can be converted into specific gravity by the formula:

$$\text{A.P.I. gravity} = \frac{141{\cdot}5}{\text{Sp. Gr.}\ \frac{60°\ \text{F}}{60°\ \text{F}}} - 131{\cdot}5$$

conversely

$$\text{Sp. Gr.}\ \frac{60°\ \text{F}}{60°\ \text{F}} = \frac{141{\cdot}5}{131{\cdot}5 \times \text{A.P.I. gravity.}},$$

For many practical purposes it is only necessary to determine the specific gravity to the third decimal place. Should, however, it be desirable to proceed to greater accuracy, then buoyancy corrections must be introduced.

The simplest method for measuring specific gravity is by a hydrometer. A hydrometer is a tubular vessel weighted at the base to enable it to remain in a vertical position when placed in the oil, and provided with a scale marked with specific gravity numbers. The hydrometer is placed in the oil, whose temperature has been adjusted to 60° F., and allowed to come to rest. The specific gravity is shown on the scale at that point at which the surface of the oil is coincident with a mark on the scale.

Should it not be convenient to adjust the temperature to 60° F. the determination can be made at other temperatures and calculating the specific gravity at 60°F. by the addition or subtraction of 0·00034 per degree Fahrenheit. When the oil is very viscous it is difficult to be certain when the hydrometer has come to rest, consequently it is probably more convenient to make the determination at a higher temperature and apply a correction.

The more accurate method is by the use of a specific gravity bottle. The bottle is filled with distilled water, and placed up to the neck in a large basin containing water which is kept at 60° F. for about thirty minutes. When the water in the bottle has acquired the correct temperature (60° F.), remove the bottle from the basin by holding it only by the neck to obviate the possibility of warming the water. The bottle is carefully dried, and the water on the stopper is very carefully removed with filter paper. It is then weighed as accurately as possible. The process is repeated, but in this case using the oil sample. From the weighings the specific gravity is calculated.

$$\text{Sp. Gr. } \frac{60^\circ \text{ F}}{60^\circ \text{ F}} = \frac{\text{Weight of oil}}{\text{Weight of water.}}$$

A convenient quantity of oil to take is about 25 ml. If, however, the oil be too viscous to weigh in this way a 100 ml. graduated flask is a more convenient vessel to use. Adjusting the level to the etched mark on the neck is not a difficult operation. By using a large volume errors are reduced.

Fig. 17.
Hydrometer.

The specific gravity of a mixture of two oils can be calculated by the formula

$$\text{Sp. Gr.} = \frac{mD_1 + nD_2}{m + n}$$

where D_1 and D_2 are the gravities of the constituent oils and m and n the proportions in which they are present in the mixture.

Sulphur is most conveniently determined by ignition in a bomb such as is used for the determination of the calorific value of fuels. Any type of bomb can be used provided no interior surface is affected by the oil or its sulphur compounds. Bombs which have been used extensively for calorific determinations may have damaged surfaces, and may therefore be unsuitable for sulphur determinations. Care should be taken that the bomb does not contain fused coal ash. For sulphur estimations in oils the capacity of the bomb should not be less than 300 ml.

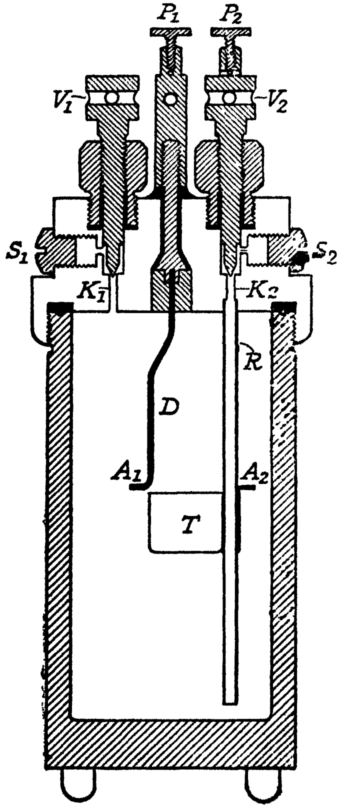


Fig. 18.—Bomb.

The oil cup may be made of platinum or silica, and should have a capacity of 2·5–5·0 ml. When a platinum cup is used it is better to use a platinum ignition wire in preference to an iron wire. To avoid using an electric current exceeding 12 volts it is convenient to employ a wire of No. 38 I.W.G. There is no specified way how the wire shall be placed to ignite the oil, but a strip of filter paper 4–5 ml. wide folded into an inverted V placed over the wire and dipping into the oil is suggested. The idea is good. Ignition is facilitated if the wire is made into a coil by winding it round a large nail. Then the wire can be half submerged in the oil. The ends are attached to the electrodes.

A quantity of oil, dried over calcium chloride, not exceeding 1 gm. is weighed into the oil cup, and then fixed into the bomb which contains 10 ml. solution of Na_2Co_3. The ignition wire and filter paper are placed in position, and the lid screwed down. Only just sufficient force to make the lid gas-tight should be used. Unnecessary violence only damages the gasket. A bomb containing a rubber gasket can now be obtained. It can be screwed down with only hand force. The bomb is charged slowly with oxygen to 25–30 atmospheres. After the valves on the bomb are closed the bomb is immersed in cold water so that the head is just covered. If there is an escape of oxygen the head must be screwed more firmly and the pressure of oxygen readjusted. Before igniting immerse the bomb into cold water. The ignition wire is heated by a 12 volt circuit for two seconds. When the bomb has cooled after the burning of the oil it is allowed to stand for about 30 minutes to ensure that the oxides of sulphur have dissolved in the water in the bomb. It is then withdrawn from the cooling bath and the gas pressure slowly released. The inside of the bomb should be free from soot and unburnt oil. Should it contain any the test must be repeated. Na_2CO_3 gives better absorption.

The aqueous solution in the bomb is transferred to a beaker, taking all the care necessary to wash out the bomb and lid with distilled water. The solution may contain particles of solid so it is filtered, and the filtrate concentrated if the volume exceeds 350 ml. To ensure that all the sulphur exists as sulphate the liquid is boiled with 2 ml. of strong hydrochloric acid and 10 ml. of saturated bromine water until all the bromine has been expelled; in fact until the total volume is approximately 75 ml. Whilst the solution is still boiling gently barium chloride is added to precipitate the sulphate as barium sulphate. Analysts have their own technique for producing barium sulphate in an easily filterable condition, and the avoidance of particles which pass the filter paper. Some add solid crystals of barium chloride, others a strong solution drop by drop. Rapid boiling after the addition or vigorous stirring is a help. Continue heating on a hot plate for about two hours. Some chemists filter whilst the solution is hot and wash with nearly boiling water, but some prefer to let the solution cool. The filter is ignited and the barium sulphate weighed. The sulphur content is obtained by calculation.

Corrosive or Deleterious Sulphur is qualitatively detected by heating the oil with bright copper foil. Corrosive or deleterious were introduced years ago to describe free or combined sulphur which were undesirable. For many classes of work the description still holds good, but with the advent of extreme pressure lubricants and sulphured cutting oils a change of view is necessary.

The generally accepted method is to heat the oil in the presence of polished copper foil at 100°C. for 3 hours in an oven. If the copper blackens, deleterious sulphur is assumed to be present. A mere colouring of the copper does not necessarily indicate sulphur.

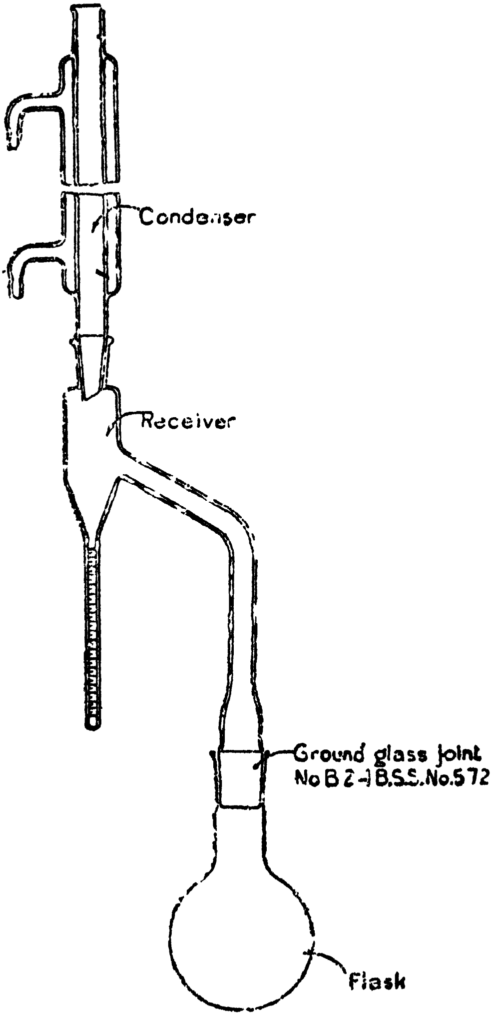


Fig. 19.

Thiocyanogen Value is a method of analysis introduced by Kaufmann in which the amount of thiocyanogen absorbed is measured in terms of iodine for convenience. This amount does not always correspond to the iodine value. It is particularly useful for measuring linolenic acid and its triglycerides in oils. The thiocyanogen radical is only absorbed at one double bond instead of at two as in the case of the iodine value. Linolenic acid absorbs thiocyanogen at two of the three double bonds. Oleic, elaidic and erucic acids show thiocyanogen values in agreement with the iodine values.

This method is mostly useful for research work.

Water is probably soluble in mineral lubricating oil to an extent less then 0·01 per cent. Therefore, if water is present it can be seen as a separate layer or as a cloudiness, or perhaps as an emulsion. A sharp cut separation enables a volumetric measurement to be made. A mere cloudiness usually indicates a very small quantity. Unfortunately there is no ready way by which the approximate amount of water in an emulsion can be gauged. An emulsion can contain 1 per cent or anything up to 95 per cent of water.

In the absence of the requisite apparatus for water-determination there may be a temptation to measure the loss of weight at 100°C., as one would do with many commodities. Such a temptation must be resisted as the results are not likely to be very useful. The standardised apparatus is so cheap and so simple to operate that it should be in all laboratories where oil testing is undertaken.

The principal difficulty in estimating water is obtaining a truly representative sample from the bulk. When water is known to be present in a large container it is usually measured in situ by the wetting of specially treated paper sold for the purpose, or its equivalent. The sample once taken it is imperative to shake it thoroughly before measuring a convenient quantity for distillation from a round-bottomed flask of 500 ml. capacity. What quantity is used is governed largely by the amount of water present. Probably 100 ml. will be convenient quantity. The measuring cylinder is rinsed with 100 ml. of petroleum spirit in successive portions, and the washings added to the flask. To the flask is attached a graduated receiver which is fitted with an efficient condenser. At the top of the condenser a plug of cotton-wool is inserted to check the ingress of moisture. The distillation is so regulated that 2 to 5 drops per second fall from the end of the condenser. The volume of water collected in the graduated receiver is noted, and the result reported as a percentage by volume.

The petroleum spirit used as a carrier must be free from water, and distil completely between 90° and 160°C., and the recovery at 100°C. shall not exceed 20 per cent when tested by I.P.–28/42. The aromatic content shall not exceed 10 per cent when tested by I.P.–3/42. Should this water spirit be difficult to obtain toluene or xylene make good substitutes provided they are saturated with water before use. Criticism has been made of the fact that as water boils at 100°C. and toluene at 110°C. there is insufficient difference between them to ensure complete carry over of the water. Provided the rate of distillation is adequate there is little to fear.

When the petroleum spirit is boiling it vaporises with the water, and is condensed in the condenser, and flows into the receiver. The water collects in the graduated limb, and the excess spirit overflows and returns to the flask. Wet oils are inclined to bump when boiled, but the danger can be obviated by the addition of small pieces of pumice. Should globules of water adhere to the inside of the condenser or receiver, it can be brought into the limb of the receiver with a fine jet of petroleum spirit.

Ground-glass joints to the apparatus are a useful refinement, but ordinary corks can be used. Rubber corks should not be employed.

Wax Test for Cable oils. The oil is placed between two glass plates separated by a ring of paper about 0·1 mm. thick. The glass plates are rectangular 9 × 10 cm., and about 1 mm. thick. The diameter of the disc of oil is about 5 cm. On both faces of the cell are placed a disc of tinfoil to which are applied an alternating potential of about 13 kilovolts. This voltage will produce an apparent stress in the oil of about 240 kv. per cm. (600 volts per mil.). The stress is applied to the oil for 72 hours at a temperature of 70°–80° C. The oven temperature is 70° C., but the oil increases in temperature due to dielectric power loss in the oil and glass. At the end of the test the glass plates are separated and the oil examined visually for wax formation. (Wax is often referred to as cheese.) It usually appears as flakes of straw colour. It is insoluble in all oil solvents. The wax is not estimated quantitively, but comparisons can be made by dissolving the treated oil in carbon tetrachloride.

An oil which forms wax in this test may be expected to form wax in cables operating at 20 kilovolts or higher. Wax in a cable will increase the power factor.

CHAPTER IX

VISCOSITY

The difference between a liquid and a solid is the ease with which their particles can be displaced. Little or no force is required to change the shape of a liquid if sufficient time is allowed for the change to occur, but force is necessary if insufficient time is permitted. This property of resisting deformation is called viscosity, and is due to the difference between the energy of translation of the molecules and the intermolecular forces between them. The molecules possess kinetic energy which keeps them in continual motion; during this motion molecular impacts occur, but owing to the proximity of the molecules in a fluid the effect of bombardment is somewhat eclipsed by the intermolecular forces. When heat is applied the molecular distances increase, consequently the intermolecular forces decrease. The loss of energy is manifested in a lowering of viscosity. It follows, therefore, that a fluid will become less viscous when its temperature is raised, unless some artificial means are applied to produce an artificial condition. In lubrication problems sometimes it is desirable to resort to the addition of rubber latex, aluminium stearate, or other substances which may be colloidal in character. An apparent anomaly is sulphur, whose viscosity increases between 150° C. and 200° C., and on further heating diminishes.

150° C.	8
200	50,000
400	150

According to Briscoe and Rinehart (*J. Phys. Chem.*, 46, 393, 1942), a solution of potassium iodide in glycerol increases its viscosity on heating. Mobile liquids, like water, have very low viscosities, mineral oils can be obtained to cover a very wide range of viscosity, and asphalt can be so viscous that it will flow eventually from a container, will support the weight of a man without visible deformation, and yet will fracture if struck with a hammer.

In order to understand the real nature of viscosity and its application to lubrication consider one of the two parallel plates separated by liquid moving in its own plane while the other is at rest. Due to friction the liquid adjacent to the moving plate moves with the same velocity as the plate and the intermediate layers of liquid move past each other with velocities proportional to their distance from the plate at rest.

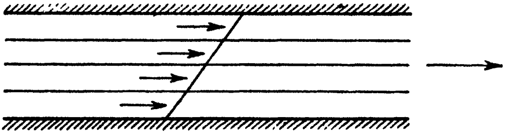


Fig. 20.

In a lubricated bearing the oil is carried round by adherence to the rotating journal. The fluid friction is produced by the film layers slipping over each other. Consider now the case of stationary boundary walls, such as a straight, narrow, cylindrical tube with liquid flowing through it. That portion of the liquid adjacent to the wall will resist the forward thrust and the intermediate layers will move with the velocities proportional to their distance from the walls.

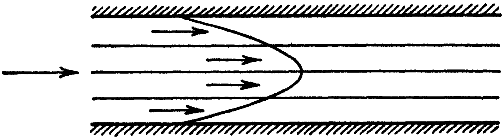


Fig. 21.

From these examples we see that there are two opposing forces, one deforming the liquid and the other resisting it. If they are equal then no motion occurs, but if the deforming force is greater, flow will result. Viscosity can therefore be expressed in terms of the deforming force. The simple definition of viscosity is the force which a surface of 1 cm² exerts on a parallel plate at a distance of 1 cm. moving with a velocity of 1 cm. per second, the space between the plates being filled with a liquid. When the force is one dyne the unit of viscosity is called a poise (*P*). For practical purposes the centipoise (*cP*) is preferred. Water at 20·2° C. has a viscosity of one centipoise, and rape oil at 20° C. about one poise. The coefficient of viscosity, or for short, viscosity, is denoted by physicists by η, but μ is commonly used by writers on hydrodynamics. In the petroleum industry kinematic viscosity has been standardised, and the unit adopted is the stoke (*s*) or centistoke (*cs*). It is denoted by ν which represents $\frac{\eta}{\rho}$, where ρ is the density (both values taken at the same temperature).

The poise is named after Poiseuille at the suggestion of Deeley and Parr (*Phil. Mag.*, 6, 26, 1913), who rediscovered independently after Hagen that the discharge of a liquid from a narrow tube is proportional to the fall of pressure per unit length and to the fourth power of the radius of the tube. Hagen, who was an engineer, appears to have been overlooked by the physicists. Hagen published his results in Poggendorff's *Annalen*, 1839, and Poiseuille in *Comptes Rendus*, 1840 and 1841. It was Jakob (*Zeit. f. techn, Physik*, 9, 21 1928), who made the proposal that the name of Stoke should be perpetuated, although of course Stoke's law will ever be remembered.

Poiseuille's investigation on viscosity led to the formula for long tubes:

$$Q = \pi P d^4 t / 128 \mu l$$

where Q is the discharge in time t in cubic centimetres; P the difference in pressure between the two ends of the tube; l the length and d the diameter of the tube in centimetres; μ the viscosity in poises.

Herschel in 1917 developed an equation for kinematic viscosity, using shorter tubes

$$\frac{\mu}{\rho} = \frac{\pi g d^4 t}{128 Q (l + \lambda)} \left(h - \frac{m v^2}{g} \right)$$

where λ the equivalent length addition due to end effects; h the head of liquid in centimetres; m the kinetic energy correction coefficient, and v the mean velocity of liquid through the tube in centimetres per second.

If the volume of discharge is kept constant the Herschel equation for a given apparatus can be simplified

$$\mu/\rho = Ct - B/t$$

To reduce errors due to the factors λ and m it is necessary to use a tube with a high l/d ratio, and a reasonably low efflux time. Thus it is only necessary to fix the efflux volume and time accurately for viscosity measurement. This simplifies the proceeding enormously. Of course careful attention must have been given to the details of the design of the viscometer which is to be used. In this country the British Standards Institution, under the guidance of Barr, has standardised the design and dimensions of the BRITISH STANDARD viscometers which are based on the Ostwald viscometer. In the U.S.A. the A.S.T.M. has approved the modification due to Fenske, and the suspended level viscometer of Ubbelohde.

The dimensions given for the British standard viscometers are abstracted from B.S.S. 188–1937.

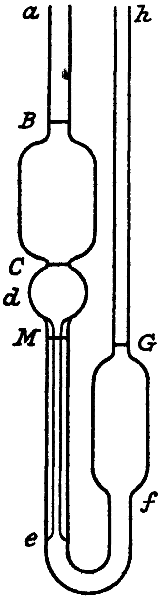


Fig. 22.

B, C, M and G are etched markings and should extend round the tube; a, d, e, f and h are for explanatory purposes only and do not appear on the viscometer.

The small bulb (Cd) serves to prevent the head of liquid being spoilt towards the end of the observation.

B.S.S. 188–1937 contains a considerable amount of useful information and is worthy of study.

For the calibration of the viscometers the following liquids are recommended as standards:

Viscometer No.	1	Water
,,	2	40 per cent sugar solution
,,	3	60 per cent ,, ,,
,,	4	No primary standard, but can be readily standardised by determining the viscosity of a liquid more viscous than the sugar solution in No. 3 and using it as a standard in No. 4.

The solutions shall be prepared by dissolving 40 and 60 grams of pure sucrose respectively in sufficient warm water to produce 100 gm. of solution. The solutions shall be filtered and their densities determined at 25°C. and corrected for buoyancy.

As the Institute of Petroleum has decided to abandon the 40 per cent sucrose solution as a primary standard no reference will be made to it here.

The calibration of the viscometers requires a good deal of skill, and a really good balance to determine the density of the solutions with the requisite degree of accuracy. Manipulating a strong solution of sugar is not simple. As the National Physical Laboratory has undertaken to provide the factor for individual viscometers chemists are advised to avail themselves of this service.

Doubtless some attention will be given to the use of 40 per cent sucrose by the B.S.I. because the results obtained with it do not always correlate satisfactorily with 60 per cent sucrose. So far no tenable explanation has been made to account for the anomalies. The Institute of Petroleum has decided to use water and 60 per cent

TABLE I

DIMENSIONS OF VISCOMETER No. 1

Range = 0·9 to 7·2 cp.
Length of Tube (aB) = 7 cm.
Length of Capillary (de) = 10 cm.
All linear dimensions are given in centimetres. All volumes are given in cubic centimetres.

Capillary (de): int. dia.	0·054	0·051	0·049	0·046	0·043	0·041
Tube (aB): int. dia.	0·30	0·25	0·20	0·15	0·10	0·10
Bulb (BC): int. dia.	1·2	1·1	1·0	0·9	0·9	0·8
capacity	1·15	0·93	0·76	0·60	0·47	0·37
Bulb (Cd): capacity	0·1	0·1	0·1	0·1	0·1	0·1
Bent tube (ef): min. int. dia.	0·3	0·3	0·3	0·3	0·3	0·3
Tube (Gh): int. dia.	0·3	0·3	0·3	0·3	0·3	0·3
Bulb (fG): min. int. dia.	1·2	1·1	1·0	1·0	0·9	0·9
min capacity	1·25	1·05	0·90	0·70	0·60	0·50
Dimension *x*	3·9	4·0	4·1	4·1	4·2	4·2
Distance between vertical axes	1·1	1·1	1·0	1·0	0·9	0·8
Vertical distance of M above G	0·6	0·6	0·7	0·7	0·8	0·8

TABLE II

DIMENSIONS OF VISCOMETER NO. 2

Range = 5·4 to 43 cp.
Length of Tube (aB) = 7 cm.
Length of Capillary (de) = 10 cm.

All linear dimensions are given in centimetres. All volumes are given in cubic centimetres.

Capillary (de): int. dia.	0·120	0·114	0·108	0·102	0·096	0·900
Tube (aB): int. dia.	0·50	0·40	0·30	0·25	0·20	0·16
Bulb (BC): int. dia.	2·0	1·9	1·7	1·6	1·5	1·4
capacity	6·5	5·3	4·3	3·4	2·7	2·1
Bulb (Cd): capacity	0·4	0·4	0·4	0·2	0·2	0·2
Bent tube (ef): min. int. dia.	0·5	0·5	0·5	0·5	0·5	0·5
Tube (Gh): int. dia.	0·5	0·5	0·5	0·5	0·5	0·5
Bulb (fG): min. int. dia.	2·0	1·9	1·7	1·6	1·5	1·5
min. capacity	7·0	5·7	4·7	3·8	3·1	2·5
Dimension x	5·6	5·5	5·3	5·2	5·1	5·1
Distance between vertical axes	1·6	1·5	1.4	1·3	1·2	1·2
Vertical distance of M above G	0·3	0·3	0·3	0·3	0·3	0·3

TABLE III

Dimensions of Viscometer No. 3

Range = 32 to 260 cp.
Length of Tube (aB) = 7 cm.
Length of Capillary (de) = 10 cm.
All linear dimensions are given in centimetres. All volumes are given in cubic centimetres.

Capillary (de): int. dia.	0·24	0·23	0·22	0·20	0·19	0·18
Tube (aB): int. dia.	0·7	0·7	0·7	0·7	0·7	0·7
Bulb (BC): int. dia.	2·8	2·6	2·4	2·2	2·1	1·9
capacity	20·0	16·2	13·2	10·4	8·2	6·4
Bulb (Cd):	1·2	1·2	1·2	0·6	0·6	0·6
Bent tube (ef): min. int. dia.	0·7	0·7	0·7	0·7	0·7	0·7
Tube (Gh): int. dia.	0·7	0·7	0·7	0·7	0·7	0·7
Bulb (fG): min. int. dia.	2·8	2·6	2·4	2·2	2·1	2·0
min. capacity	21·5	18·0	15·0	11·5	9·0	7·5
Dimension *x*	5·7	5·5	5·3	5·1	5·0	4·9
Distance between vertical axes	2·1	2·0	1·8	1·6	1·5	1·4
Vertical distance of M above G	0·12	0·12	0·12	0·15	0·15	0·15

TABLE IV

DIMENSIONS OF VISCOMETER NO. 4

Range = 190 to 1,500 cp.
Length of Tube (aB) = 7 cm.
Length of Capillary (de) = 10 cm.

All linear dimensions are given in centimetres. All volumes are given in cubic centimetres.

Capillary (de): int. dia.	0·4	0·38	0·36	0·34	0·32	0·30
Tube (aB): int. dia.	0·7	0·7	0·7	0·7	0·7	0·7
Bulb (BC): int. dia.	3·2	3·2	3·1	2·9	2·6	2·4
capacity	32·0	26·0	21·0	17·0	13·0	10·0
Bulb (Cd): capacity	1·4	1·4	1·3	1·0	0·8	0·8
Bent tube (ef): min. int. dia.	0·8	0·8	0·8	0·8	0·8	0·8
Tube (Gh):	0·8	0·8	0·8	0·8	0·8	0·8
Bulb (fG): min. int. dia.	3·2	3·2	3·2	2·9	2·6	2·5
min. capacity	33·5	27·5	22·5	18·5	14·0	11·0
Dimension *x*	7·1	7·1	7·0	6·8	6·5	6·3
Distance between vertical axes	2·3	2·3	2·2	2·0	1·7	1·5
Vertical distance of M above G	0·1	0·1	0·1	0·1	0·1	0·1

sucrose only as primary standards now that such a high degree of accuracy for viscosity measurements is being developed.

"60 PER CENT" SUCROSE SOLUTION

Density	Viscosity	Density	Viscosity	Density	Viscosity	Density	Viscosity
1·28275	42·56	1·28340	43·25	1·28405	43·95	1·28470	44·67
1·28280	42·61	1·28345	43·30	1·28410	44·00	1·28475	44·73
1·28285	42·66	1·28350	43·35	1·28415	44·06	1·28480	44·78
1·28290	42·71	1·28355	43·41	1·28420	44·11	1·28485	44·84
1·28295	42·77	1·28360	43·46	1·28425	44·17	1·28490	44·89
1·28300	42·82	1·28365	43·52	1·28430	44·22	1·28495	44·95
1·28305	42·87	1·28370	43·57	1·28435	44·28	1·28500	45·01
1·28310	42·92	1·28375	43·63	1·28440	44·33	1·28505	45·07
1·28315	42·98	1·28380	43·68	1·28445	44·39	1·28510	45·12
1·28320	43·03	1·28385	43·74	1·28450	44·45	1·28515	45·18
1·28325	43·09	1·28390	43·79	1·28455	44·51	1·28520	45·23
1·28330	43·14	1·28395	43·84	1·28460	44·56	1·28525	45·29
1·28335	43·20	1·28400	43·89	1·28465	44·62	—	—

NOTE.—The data in the above tables are based upon the measurements recorded in Scientific Paper * 298–1917 of the Bureau of Standards, Washington, U.S.A., from which they have been interpolated by means of the following formula:

$\log \eta = 1{\cdot}95134 + 2{\cdot}9728x + 3{\cdot}2212x^2 + 24{\cdot}254x^3.$
where η = viscosity in cp. at 25° C.
and $x = \rho$ density of solution at 25° C.
ρw = density of water at 25° C. = 0·99707.

* Paper by Bingham and Jackson.

The FENSKE viscometer has bulb C in line with bulbs A and B, in order to reduce errors due to deviation from the vertical. Bulb A is added to reduce variations in volume of liquid in the viscometer. The use of a large bulb C together with bulb A practically eliminates any errors due to variations in pressure. The dimensions and minimum efflux time are selected so as to make the kinetic energy effect insignificant. The constant B in equation $\mu/\rho = Ct + B/t$ is assumed to be zero. The instrument is charged by inverting the tube above the bulb A into the oil for test and applying suction to the tube above bulb C. This procedure introduces the difficulty that the operator cannot check the volume of liquid in the viscometer once it has been filled to the mark below bulb B.

The UBBELOHDE suspended level viscometer obviates any error due to filling since the effective head of liquid depends only on the height of the liquid from a point in the suspended level, and does not depend at all on the height of the liquid in the other limb of the viscometer. Any error due to deviation from the vertical is reduced by placing the suspended level directly under the upper bulb. This type of viscometer avoids any bottom bulb errors, but on the other hand, top bulb errors are not compensated in the lower bulb. In the suspended level types with spherical shoulder, differences due to surface tension in the liquids examined are eliminated. The calibration of these instruments is generally based on pure distilled water for viscometers with a capillary diameter less than 0·75 mm. and on secondary oil standards for capillary diameters greater than 0·75 mm.

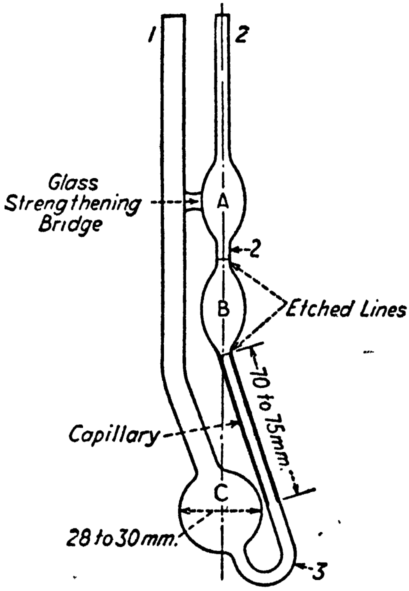


Fig. 23.—Fenske Viscometer.

Although prominence has been given to the three viscometers which scientists are determined to use, complete neglect of the three instruments of commerce cannot be permitted yet. The Redwood, Saybolt and Engler instruments have been used for years in England, U.S.A. and Germany respectively. In France the Barbey Ixometer is happily almost defunct. The petroleum industry thinks in terms of these three, and practically the whole output of mineral oils is sold on their units. To change the units of commerce is a gigantic task, because people's minds have crystallised in those shapes, and are not easily recrystallised. But as the change must come let it come quickly to avoid a confused transition stage.

The Redwood viscometer consists of a silvered copper oil cylinder furnished with an agate jet. The oil cylinder is screwed into a copper bath which serves as a temperature regulator, heat being applied to a tube projecting from the side. A revolving agitator is placed in the bath. The oil cylinder is furnished with a valve consisting of a small brass sphere attached to a wire, which rests in a hemispherical cavity in the agate jet. Inside the cylinder, at a short distance from the top, is fixed a small bracket with an upturned point to indicate the oil level. The instrument is supported on a tripod provided with levelling screws.

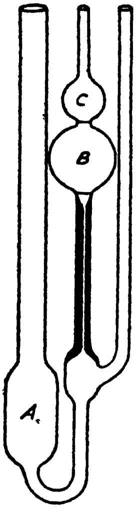


Fig. 24.—Ubbelohde Viscometer.

The bath is filled with a suitable liquid to a height roughly corresponding with the point of the gauge in the oil cylinder. Water may be used for temperatures up to 200°F., and mineral oil for higher temperatures. The oil to be tested is placed in the oil cylinder, and its temperature adjusted to that at which the determination is to be made, by regulating the liquid in the outer vessel to such a temperature as will maintain the oil at the desired temperature. In very hot weather the temperature of the outer liquid should be kept at 69·5°F. to maintain a constant temperature of the oil at 70°, and at 70·5° in very cold weather. When the temperature of the estimation is 140° the heating liquid should be about 142°, and at

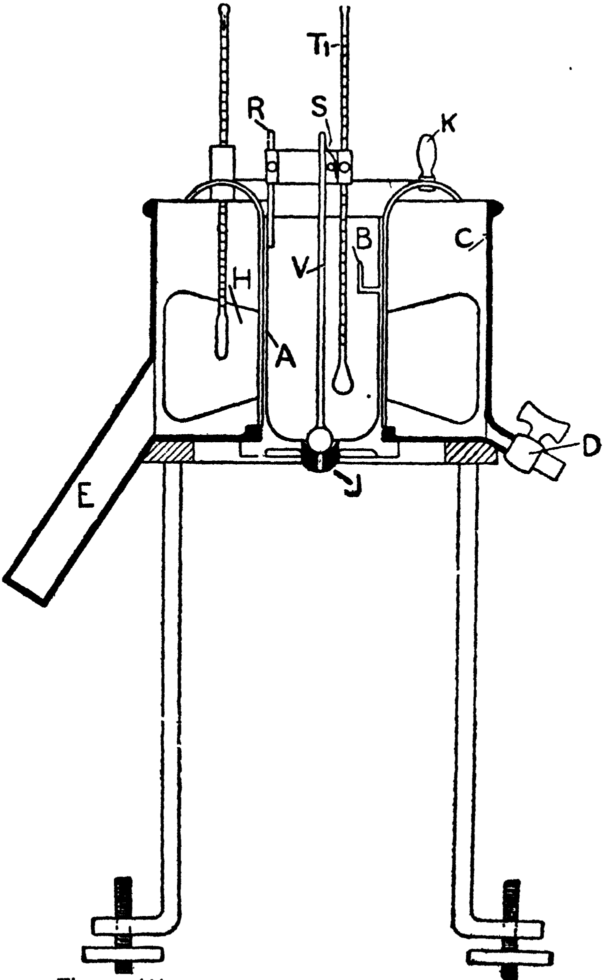


Fig. 25. (A)—The Redwood Viscometer. No. 1.

higher temperatures corresponding differences. These temperature differences are necessary to compensate for the heat variations at the base and surface of the oil. The oil in the cylinder is stirred by moving the thermometer backwards and forwards in the oil, but in a manner to avoid the formation of air bubbles, and fracture of the thermometer. The outer liquid should be kept well stirred. The efficient stirring of the outer liquid and the oil is the secret of rapid determinations. When the temperature has become constant allow

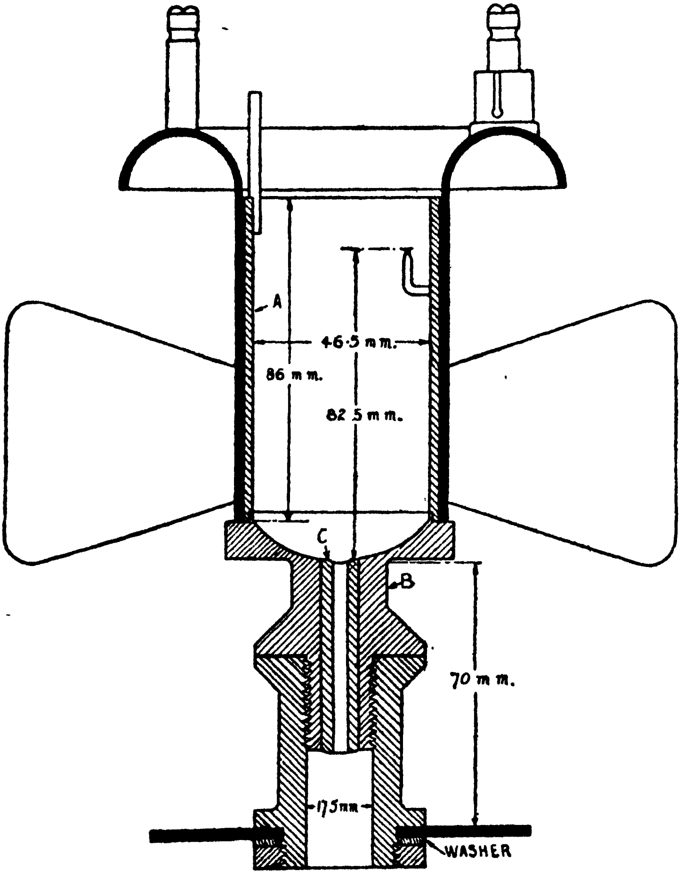


Fig. 25. (B)—The Redwood Viscometer. No. 2.

the oil to remain undisturbed for a few minutes to release air bubbles and currents, after which no stirring shall be done. Then adjust the level of the oil to the point of the gauge.

Fix the thermometer which is in the oil about half-way between the wall and the centre of the cylinder. A cover is placed on the oil cylinder to assist in maintaining a constant temperature. Then the ball valve is lifted and secured on the thermometer holder, a stopwatch started simultaneously, and the time noted for the efflux of exactly 50 ml.

STANDARD DIMENSIONS OF REDWOOD NO. 1 VISCOMETER

	Normal mm.	Tolerance mm.
Internal diameter of oil cylinder	46·5	0·5
„ height of cylindrical portion	90·0	±0·25
Height of filling point above upper end of jet	82·5	±2·00
Internal height of jet	10·0	±0·02
„ diameter of jet	1·6	±0·01

The capacity of the oil cylinder is approximately 135 ml.

The repeatability of determinations by individual operators with the same apparatus should be within one per cent of the mean value in Redwood seconds.

The viscosity is recorded in seconds at a specified temperature. The Institute of Petroleum recommends that determinations shall be made at 70°, 140° and 200°F. for the sake of uniformity.

As this instrument is only suitable for efflux times between 50 and 3,000 seconds, a larger instrument is available, described as Redwood No. 2, for more viscous oils. It is so designed that the efflux time is one-tenth of Redwood No. 1.

Those laboratories which do not possess a viscometer are recommended to adopt the kinematic viscometer forthwith, and convert to Redwood seconds if necessary.

Let it be remembered that viscosity measurements can be vitiated by foreign bodies. It is necessary, therefore, to be sure that contamination does not occur. The oil should be filtered before use, and water discarded; further, the oil cylinder should be carefully cleaned before use. A convenient filter is made from 100 mesh wire gauze, or fine muslin free from detachable fibres. How the cylinder shall be cleaned is optional, but tissue paper or fine muslin is convenient. Do not forget the agate jet.

Occasionally oils are encountered whose viscosity do not remain constant at any one temperature below 120°F. The change in viscosity may be due to the heat treatment of the oil, although some oils change their viscosity on standing for prolonged periods at atmospheric temperature. To adopt a uniform method for dealing with oils which exhibit this hysteresis the Institute of Petroleum has recommended that the oil be heated for one hour at 212°F., allowed to cool, and kept at 60°F. for 24 hours before testing. Whilst this precaution facilitates uniformity with many abnormal oils, it certainly aggravates the difficulty with some black oils. Unfortunately there is no known method for circumventing the trouble with this type of oil. Fortunately, however, it is rare.

Saybolt Viscometer finds favour in the United States of America. In principle it is similar to the Redwood instrument and with it must be regarded as a commercial viscometer. Like the Redwood it exists in two modifications known as Universal and Furol.

Dimensions of Saybolt Universal Viscometer

	Min.	Normal	Max.
Inside diameter of outlet tube	0·1750 cm.	0·1765 cm.	0·1780 cm.
Outside diameter of outlet tube at lower end	0·28	0·30	0·32
Length of outlet tube	1·215	1·225	1·235
Height of overflow rim above bottom of outlet tube	12·40	12·50	12·60
Outside diameter of overflow rim at the top	3·20	—	3·30
Diameter of container	2·955	2·975	2·995
Depth of cylindrical part of container	8·8	—	—
Diameter of container between bottom of cylindrical part of container and top of outlet tube	0·9	—	—

The oil tube A is fitted at the top with an overflow cup, and the tube is surrounded by a bath. At the bottom of the oil tube is a small outlet tube through which the oil to be tested flows into a receiving flask whose capacity at 20°C. (68°F.) to a mark on its neck is 60 ml. ± 0·15 ml. The outlet tube is of hard and corrosion resisting metal, such as stainless steel, Monel metal, etc. The lower end of the outlet tube is enclosed by a larger tube, which when stoppered by a cork prevents the flow of oil through the outlet tube until the cork is removed. The bath may be heated by any convenient means.

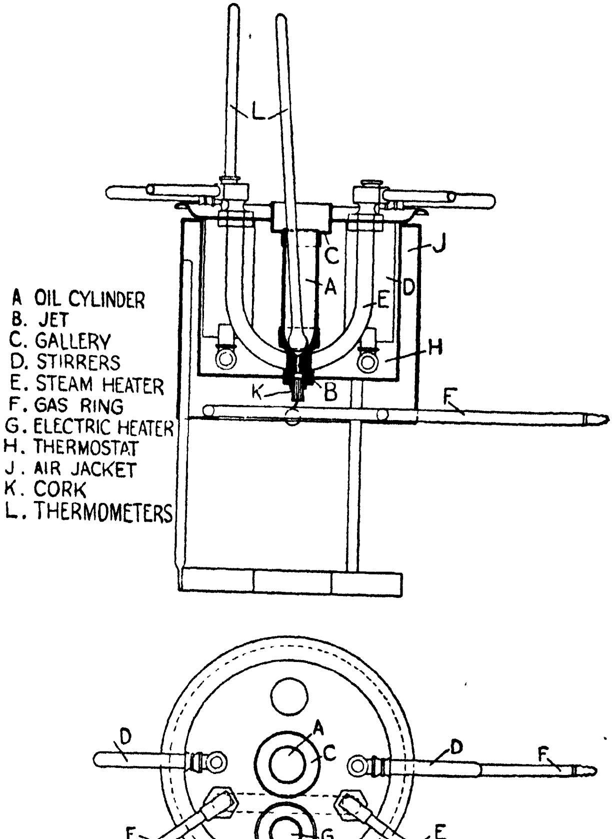


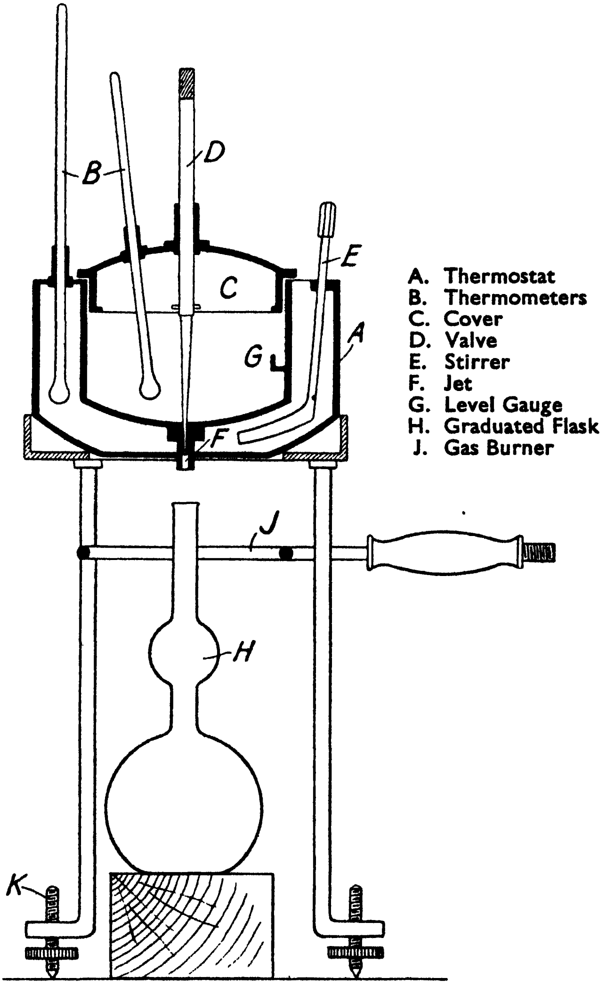
Fig. 26.—Saybolt Viscometer.

Before commencing the test it is useful to pour some of the oil through the viscometer to flush the capillary. The viscometer is then filled so that oil overflows into the overflow cup. After the temperature is adjusted oil in the overflow cup is withdrawn, and a stop-watch started after the flask is in position. The number of seconds required for the efflux of 60 ml. is recorded as the viscosity.

The determinations are made at 100° and 210°F.

Precautions enumerated under the heading of Redwood viscometer must be taken where applicable.

In the U.S.A. the Saybolt viscometer is being replaced by kinematic viscometers.



A. Thermostat
B. Thermometers
C. Cover
D. Valve
E. Stirrer
F. Jet
G. Level Gauge
H. Graduated Flask
J. Gas Burner

Fig. 27.—The Engler Viscometer.

The **Engler** viscometer is mainly used in Germany. It consists of two metal basins, one placed within the other, one serving as an oil reservoir and the other as a thermostat. The oil bath is fixed into the thermostat by supports and by the discharge pipe F. A valve pin D passed through the lid and seats in the discharge pipe. Three needle-point gauges are fixed in the oil bath equidistant from the bottom for measuring the oil on the one hand, and, on the other, to serve for the correct adjustment of the horizontal position of the apparatus. When the oil bath is filled to gauge level it should contain 240 ml. A tripod supports the apparatus. A measuring flask having on its neck two marks, one registering 200 ml., the other 240 ml., is placed under the platinum discharge tube when a determination is to be made.

To test the correctness of the apparatus the time taken for 200 ml. of water at 20° C. to flow out of the oil bath, when it is filled to the gauges, is noted. Before removing the valve the water should be allowed to acquire a state of rest after being stirred by rotating the lid with the thermometer in position. Exactly the same procedure is adopted when an oil is being tested.

The Engler degree of viscosity is obtained by dividing the number of seconds required for the outflow of 200 ml. of oil by the time for the outflow of an equal volume of water at 20° C.

Results may vary as much as 7 per cent with this viscometer.

A number of other viscometers have been used, but as the kinematic viscometers are now being widely adopted a description is not necessary.

Attention has been given to the determination of viscosity under high pressures for the reason given in the chapter on Friction and Lubrication. A word of warning, however, is desirable when considering very thin films. Any variation of the lubricant due to pressure must be of the greatest importance in lubrication, but what is under consideration is not the variation of the viscosity of the lubricant in mass, but the effect of pressure upon the peculiar constraints exercised by the attractive forces of the bounding solids. The fact that the viscosity of a lubricant in mass increases with increasing pressure cannot be held to prove that the viscosity of a film a few molecules thick with its molecules highly orientated will be changed in a similar way by pressure.

Hyde stated that all oils tested by him at the N.P.L. showed a rapid increase in viscosity with pressure, but the increase was far greater for the mineral oils than for animal and vegetable oils. At 8 tons pressure castor had increased to 5·5 times, whereas mineral oil was about 20 times. Of course it has long been known that oils lose viscosity when heated, but it is less commonly known that oils increase in viscosity under pressure. The viscosity of the oil led into a bearing is not necessarily the viscosity at the point of highest pressure. Through frictional heat it may have become thinner, and if the pressure is sufficiently high it may become thicker. The two influences may cancel out. If this increase in viscosity could be properly used it is conceivable that bearings of many times their present capacity could be produced. This is no fantastic notion; already the development is in that direction as is evidenced by the Michell bearing. With comparatively thick films the pressure-viscosity effect is small, but as the thickness is reduced the effect becomes marked. Smoothness of bearing and journal are essential to success. It is not beyond the power of engineers to meet the requirements of machining and alignment. Bradford and Vandegrift (Gen. Dis., 1937) determined the coefficient of friction in a bearing supplied with lard oil, and with a Penna oil, of equal viscosity at the assumed temperature and atmospheric pressure, the pressure within the bearing was increased by stages. The curves show that: (1) the two oils give different coefficients of friction for the same load; (2) the coefficient for lard is the lower; (3) the differences are greatest in the high-pressure region. They claim that the difference in this case is solely due to the pressure-viscosity effect and not to any mysterious property called oiliness.

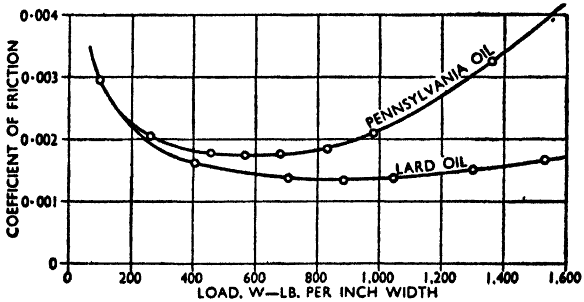


Fig. 28.

In view of the certain transition from commercial viscometers to kinematic viscometers it is reasonable to anticipate opposition. Many people have become accustomed to think in established units, and they will find it difficult to make a complete change, and perhaps they will be reluctant to do so unless they understand why the change is desirable or necessary. The change is no mere fashion set by scientists. It is a logical step in the path of progress. It is nearly sixty years ago since the Redwood type of instrument was invented. For about forty years it was accepted without serious challenge. But twenty years ago the petroleum industry had made a real start on the application of scientific principles to ensure its development, and was giving earnest consideration to the standardisation of tests for petroleum products. The Redwood instrument came under review, and its deficiencies revealed. Serious efforts were made to improve its accuracy by standardisation of dimensions and calibration. In fact instrument No. 1307 was housed at the N.P.L. and adopted as the master Redwood instrument. Should this master standard be destroyed some embarrassment must follow. However much energy is expended upon its improvement a really accurate instrument could never be achieved, because its design is fundamentally unsound in several respects. Therefore it is better that it should be superseded by a viscometer which gives a greater degree of repeatability, and is based upon more nearly scientific principles.

VISCOSITY INDEX

The need for greater accuracy has become necessary with the establishment of viscosity index. To obtain viscosity index within a few points demands a viscosity accuracy within about ±0·3 per cent, particularly with thin oils. Cragg and Evans (*J. Inst. Pet.*, 1943, 29, 99) have calculated the effect on viscosity index by viscosity errors.

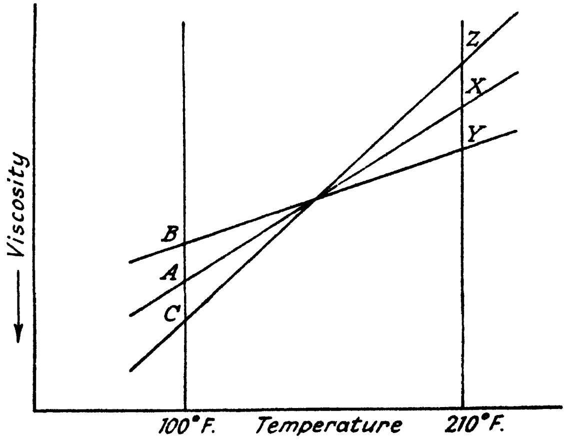
POSSIBLE DEVIATION FROM MEAN IN V.I. UNITS FOR STATED VISCOSITY ERROR

Viscosity at 210° F Centistokes	0·25%		0·5%		1%		2%	
	V.I. 0	V.I. 100	V.I. 0	V.I. 100	V.I. 0	V.I. 100	V.I. 0	V.I. 100
2·0	3	3	6	5	12	9	24	18
4·0	3	2	6	4	12	7	23	13
6·0	2	1	4	3	8	5	16	9
8·0	2	1	4	2	7	3	13	7
12·0	2	1	3	1	6	3	11	5
20·0	1	1	2	1	5	2	10	4

The meaning of this table is made clearer by a diagram.

From this it will be clear the degree of accuracy it is necessary to attain to meet specified deviations in V.I. For thick oils a tolerance of ±1 per cent may be permissible, but for a thin oil an error of ±0·25 per cent should be the goal. For practical purposes very high degrees of accuracy have not been called for, but as viscosity index has a possible commercial importance attention must be given to the degree of accuracy with which it can be estimated. Perhaps too much importance is being attached to the subject. Be that as it may, the subject is there and must be tackled.

The subject has received a lot of consideration, and now it is fully realised that it has many difficulties, in fact far more than was anticipated a year or two ago. A thermostat capable of constant control to 0·025°F. is the first requisite. The bath should be of large capacity, circular, and fitted with a very efficient high-speed stirrer, with the bottom screw throwing the water up, and the top screw casting it down. Even though a suitable electrical control circuit is provided, and carefully operated, a voltage control may become necessary if there are electrical devices in the neighbourhood which cause fluctuations in the circuit. Whilst it may not be essential to rely on a N.P.L. certified thermometer reading to 0·02°F. it is strongly recommended. Design and dimensions of the viscometer are of paramount importance. Variations from the tolerances may lead to results in different calibration constants with different times of flow. Calibration of the viscometer must be done very carefully so that the error does not exceed ±0·3 per cent. The primary standard can be water or 60 per cent sucrose for the No. 1 and No. 3 B.S. viscometers respectively. The calibration constants for No. 2 and No. 4 are obtained by stepping up or down from the



AB, AC, XY, and XZ represent stated viscosity error (*x* per cent).
AX represents the viscosity characteristics giving the true or mean V.I.
BY represents the viscosity characteristics giving the maximum V.I. obtainable with an error of *x* per cent.
CZ represents the viscosity characteristics giving the minimum V.I. obtainable with an error of *x* per cent.

Fig. 29.

No. 1 and No. 3. For the suspended level viscometers water is recommended. Water is usually assumed to have a viscosity of 1·007 cs. at 68°F., and 0·689 cs. at 100°F., when determining the calibration constant of suspended level viscometers. In the U.S.A. the A.P.I. and the Bureau of Standards have secondary oil standards which simplify considerably calibration.

In this country the Institute of Petroleum recognises a maximum calibration error of ±0·3 per cent for an individual viscometer, and an additional ±0·3 per cent on the viscosity determination of an oil sample.

In days gone by it was customary to express the temperature-viscosity of an oil by such indefinite expressions as steep curve or flat curve. Those people who wished to be more definite stated the viscosity at one temperature and the ratio at another. For specifications this system is good. Plotting viscosity on linear graph paper has long been practised, the curves were roughly hyperbolic in shape. To approach more nearly to a straight line logarithmic paper was introduced. In 1932 the A.S.T.M. adopted a chart based on an empirical equation. Log log $(cs+0{\cdot}8)=A \log T+B$, where T is the absolute temperature and A and B are constants. Later this chart was slightly revised using log log $(cs+0{\cdot}6)=A \log T+B$. This paper is used extensively for obtaining viscosities of oils at low temperatures by extrapolation, but of course not below their pour points. In this country R.E.F.U.T.A.S. viscosity-temperature charts by Kelly are often used.

At the pour point, oils do not all have the same viscosity. The following table contains the determined viscosities to illustrate the type of variation which occurs. Four separate oils were cooled and the flow time measured in a B.S.I. No. 4 viscometer and in a Redwood No. 2.

Redwood No. 1 at 140°F.	B.S.I. No. 4	Redwood No. 2	B.S.I. No. 4	Redwood No. 2	Pour Point
	(*a*)	(*a*)	(*b*)	(*b*)	
132″	1800″	6240″	3300″	11520″	5°F.
165″	6180″	21920″	4800″	16680″	10°F.
245″	7200″	24960″	6600″	22920″	10°F.
245″	18000″	62460″	7200″	24000″	10°F.

(*a*) after cooling overnight in refrigerator at 3° F;
(*b*) immediately after cooling in a freezing mixture at 10° F.

The fourth oil contained 5 per cent of rape oil. From this result it appears that some compounded oils increase in viscosity more than do mineral oils. In dealing with compounded oils it is well to bear in mind that crystallisation of glycerides might occur at temperatures well above the pour point of the oil. When this happens an anomalous viscosity will be observed.

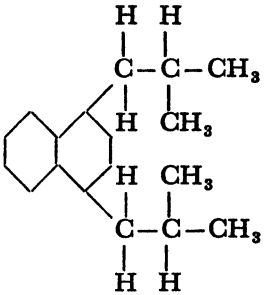
Graph papers have found extensive use, but they have limitations if they are not used intelligently. Before plotting it is necessary to be sure that the viscosities at the two or more temperatures shall be accurately determined. If any error is made the line joining the points will be the wrong slope, and any error on extrapolation will be magnified. Viscosity by extrapolation at low temperatures may be far from the true figure if the points are not exactly at the proper place. Even the thickness of the line may interfere with accuracy.

The graphical method must be regarded as a convenience, and not as an alternative to direct measurement.

A number of expressions have been suggested for the calculation of viscosity at different temperatures, but they are mainly of academic interest. It is approximately true to state that, between 20° and 120° C., the coefficient of viscosity of most oils varies as the 2·6 power of the temperature ($\eta \times t^{2\cdot 6}$ constant). To solve this difficulty of expressing the viscosity-temperature relationship Dean and Davis (*Chem. Eng. Met.*, 36, 618, 1929) introduced a scheme by which a single number, called viscosity index, classifies an oil according to its viscosity-temperature characteristic. By this scheme an oil which loses viscosity rapidly with temperature has a low viscosity index, and an oil with a minimum change a high V.I. They selected two sets of oil having big and little change respectively. The one with the big change they gave a V.I. of 0, and to the other a V.I. of 100. From the various types of oil available at that time they selected the Texas Coastal oils to represent the lowest V.I. and Penna oils for the highest V.I. Clearly any oils having a viscosity-temperature curve between these two types must have a V.I. somewhere between 0 and 100. Since that date, however, other oils have appeared, some of which have a V.I. below 0 and some above 100. Needless to say the V.I. is governed by the type of hydrocarbons in the oil.

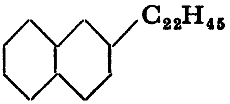
To illustrate how V.I. can be affected by chemical composition two compounds have been chosen, one with an extremely low V.I. and the other with a very high V.I.

1 : 4 di-isobutyl naphthalene, $C_{18}H_{24}$



Mol. Wt.	Sp. Gr. at 60° F.	Saybolt 100° F.	Saybolt 210 F°.	V.I.
240	0·936	74·5	34·4	–284

β-duocosayl naphthalene, $C_{32}H_{52}$



Mol. Wt.	Sp. Gr. at 60° F.	Saybolt 100° F.	Saybolt 210° F.	V.I.
436	0·905	168·0	47·6	144

Dean and Davis prepared tables giving the viscosities at 100°F. and 210°F. of the Coastal oils (L) and the Penna oils (H). The viscosity index of an oil can be calculated from the equation

$$\text{V.I.} = \frac{L-U}{L-H} \times 100 \quad \text{or} \quad \text{V.I.} = \frac{L-U}{D} \times 100$$

where V.I.=viscosity index, U=viscosity at 100°F. of the oil whose V.I. is to be calculated, L and H=respectively the viscosities at 100°F. of the series, L and H oils having the same viscosity at 210°F. as the oil U.

Now that kinematic viscosity is being widely used tables have been prepared giving kinematic viscosities for the purpose of calculating viscosity index. The tables printed in these pages are copied from I.P. Standards, Standard Methods for Testing Petroleum and its Products, 1944.

The conversion of the results from one viscometer into another is complicated by the different temperatures at which the determinations are made. Redwood viscosities are usually measured at 70°, 140° and 200°F.; Saybolt at 100° and 210°F., and Engler at 20° and 50°C. Consequently any conversion which is made obviously refers only to the one specific temperature, but by plotting

TABLE V

Values of H, L, *and* D *for Kinematic Viscosity in Centistokes at* 210° *F.*

H = Viscosity at 100° F. of an oil of 100 viscosity index.
L = Viscosity at 100° F. of an oil of 0 viscosity index.

Kinematic viscosity at 210° F., centi-stokes	*H*	*L*	*D* (*L*—*H*)	Kinematic viscosity at 210° F., centi-stokes	*H*	*L*	D (*L*—*H*)
2·00	6·620	8·360	1·740	6·00	40·630	62·430	21·800
2·10	7·143	9·043	1·900	6·10	41·690	64·430	22·740
2·20	7·684	9·752	2·068	6·20	42·750	66·430	23·680
2·30	8·243	10·485	2·242	6·30	43·810	68·430	24·620
2·40	8·821	11·244	2·423	6·40	44·880	70·430	25·550
2·50	9·417	12·028	2·611	6·50	45·970	72·460	26·490
2·60	10·031	12·838	2·807	6·60	47·080	74·550	27·470
2·70	10·664	13·672	3·008	6·70	48·220	76·740	28·520
2·80	11·315	14·532	3·217	6·80	49·390	79·040	29·650
2·90	11·984	15·417	3·433	6·90	50·590	81·440	30·850
3·00	12·671	16·328	3·657	7·00	51·820	83·920	32·100
3·10	13·377	17·263	3·886	7·10	52·980	86·460	33·480
3·20	14·101	18·224	4·123	7·20	54·150	89·040	34·890
3·30	14·843	19·210	4·367	7·30	55·273	91·660	36·387
3·40	15·603	20·222	4·619	7·40	56·473	94·095	37·622
3·50	16·382	21·258	4·876	7·50	57·669	96·528	38·859
3·60	17·179	22·320	5·141	7·60	58·873	98·958	40·085
3·70	17·994	23·407	5·413	7·70	60·063	101·398	41·335
3·80	18·828	24·520	5·692	7·80	61·305	103·925	42·620
3·90	19·680	25·657	5·977	7·90	62·513	106·388	43·875
4·00	20·550	26·820	6·270	8·00	63·723	108·859	45·136
4·10	21·400	28·060	6·660	8·10	64·969	111·419	46·450
4·20	22·280	29·360	7·080	8·20	66·251	114·067	47·816
4·30	23·180	30·730	7·550	8·30	67·501	116·650	49·149
4·40	24·100	32·180	8·080	8·40	68·753	119·306	50·553
4·50	25·040	33·720	8·680	8·50	70·041	121·926	51·885
4·60	26·000	35·350	9·350	8·60	71·296	124·528	53·232
4·70	26·980	37·060	10·080	8·70	72·542	127·153	54·611
4·80	27·980	38·840	10·860	8·80	73·793	129·786	55·993
4·90	29·000	40·680	11·680	8·90	75·089	132·515	57·426
5·00	30·040	42·570	12·530	9·00	76·352	135·176	58·824
5·10	31·090	44·500	13·410	9·10	77·617	137·841	60·224
5·20	32·150	46·460	14·310	9·20	78·880	140·517	61·637
5·30	33·210	48·440	15·230	9·30	80·184	143·284	63·100
5·40	34·270	50·430	16·160	9·40	81·448	145·989	64·541
5·50	35·330	52·430	17·100	9·50	82·714	148·695	65·981
5·60	36·390	18·040	18·040	9·60	83·986	151·411	67·425
5·70	37·450	56·430	18·980	9·70	85·262	154·147	68·885
5·80	38·510	58·430	19·920	9·80	86·575	156·982	70·407
5·90	39·570	60·430	20·860	9·90	87·856	159·722	71·866

TABLE V—*continued*

Kinematic viscosity at 210° F., centi-stokes	*H*	*L*	*D* (*L*—*H*)	Kinematic viscosity at 210° F., centi-stokes	*H*	*L*	*D* (*L*—*H*)
10·00	89·178	162·494	73·316	14·00	146·402	292·388	145·986
10·10	90·458	165·361	74·903	14·10	147·933	296·014	148·081
10·20	91·814	168·303	76·489	14·20	149·507	299·749	150·242
10·30	93·128	171·194	78·066	14·30	151·043	303·402	152·359
10·40	94·461	174·075	79·614	14·40	152·582	307·069	154·487
10·50	95·825	177·068	81·243	14·50	154·124	310·749	156·625
10·60	97·152	179·980	82·828	14·60	155·708	314·540	158·832
10·70	98·492	182·907	84·415	14·70	157·255	318·247	160·992
10·80	99·818	185·849	86·031	14·80	158·804	321·968	163·164
10·90	101·206	188·873	87·667	14·90	160·396	325·801	165·405
11·00	102·537	191·848	89·311	15·00	161·950	329·549	167·599
11·10	103·909	194·899	90·990	15·10	163·548	333·410	169·862
11·20	105·305	197·966	92·661	15·20	165·190	337·385	172·195
11·30	106·721	201·150	94·429	15·30	166·793	341·275	174·482
11·40	108·100	204·238	96·138	15·40	168·399	345·179	176·780
11·50	109·493	207·339	97·846	15·50	170·007	348·881	178·874
11·60	110·887	210·468	99·581	15·60	171·660	353·131	181·471
11·70	112·273	213·601	101·328	15·70	173·274	357·078	183·804
11·80	113·711	216·829	103·118	15·80	174·891	361·039	186·148
11·90	115·114	219·981	104·867	15·90	176·552	365·117	188·565
12·00	116·507	223·145	106·638	16·00	178·174	369·107	190·933
12·10	117·948	226·412	108·464	16·10	179·841	373·214	193·373
12·20	119·438	229·784	110·346	16·20	181·552	377·439	195·987
12·30	120·883	233·078	112·195	16·30	183·224	381·577	198·353
12·40	122·330	236·392	114·062	16·40	184·942	385·729	200·787
12·50	123·781	239·713	115·932	16·50	186·577	389·897	203·320
12·60	125·274	243·136	117·862	16·60	188·300	394·184	205·884
12·70	126·730	246·482	119·752	16·70	189·983	398·381	208·398
12·80	128·189	249·842	121·653	16·80	191·670	402·594	210·924
12·90	129·689	253·305	123·616	16·90	193·401	406·929	213·528
13·00	131·153	256·690	125·537	17·00	195·094	411·172	216·078
13·10	132·658	260·180	127·522	17·10	196·831	415·537	218·706
13·20	134·166	263·684	129·518	17·20	198·571	419·917	221·346
13·30	135·716	267·293	131·577	17·30	200·357	424·421	224·064
13·40	137·230	270·824	133·594	17·40	202·104	428·832	226·728
13·50	138·745	274·369	135·624	17·50	203·853	433·260	229·407
13·60	140·270	277·964	137·694	17·60	205·605	437·704	232·099
13·70	141·784	281·498	139·714	17·70	207·361	442·161	234·800
13·80	143·348	285·177	141·829	17·80	209·162	446·745	237·583
13·90	144·874	288·776	143·902	17·90	210·923	451·237	240·314

TABLE V—*continued*

Kinematic viscosity at 210° F., centi-stokes	*H*	*L*	*D* (*L*—*H*)	Kinematic viscosity at 210° F., centi-stokes	*H*	*L*	*D* (*L*—*H*)
18·00	212·687	455·743	243·056	24·00	328·63	768·00	439·37
18·10	214·350	460·266	245·916	24·20	332·45	778·76	446·31
18·20	216·268	464·915	248·647	24·40	336·75	790·92	454·17
18·30	218·042	469·469	251·427	24·60	341·05	803·17	462·12
18·40	219·818	474·039	254·221	24·80	345·40	815·49	470·09
18·50	221·597	478·625	257·028	25·00	349·3	826·5	477·2
18·60	223·423	483·339	259·916	25·20	353·6	839·0	485·4
18·70	225·208	487·956	262·748	25·40	358·0	851·5	493·5
18·80	226·996	492·590	265·594	25·60	362·4	864·1	501·7
18·90	228·831	497·352	268·521	25·80	366·8	876·8	510·0
19·00	230·625	502·017	271·392	26·00	371·2	889·6	518·4
19·10	232·466	506·812	274·346	26·20	375·1	901·0	525·9
19·20	234·354	511·739	277·385	26·40	379·6	913·9	534·3
19·30	236·201	516·568	280·367	26·60	384·0	926·9	542·9
19·40	238·052	521·413	283·361	26·80	388·5	939·9	551·4
19·50	239·906	526·274	286·368	27·00	393·0	953·1	560·1
19·60	241·806	531·247	289·441	27·20	397·5	966·3	568·8
19·70	243·666	536·164	292·498	27·40	402·0	979·6	577·6
19·80	245·529	541·075	295·546	27·60	406·0	991·4	585·4
19·90	247·440	546·120	298·680	27·80	410·6	1004·9	594·3
20·00	249·31	551·07	301·76	28·00	415·1	1018·4	603·3
20·20	253·10	561·12	308·02	28·20	419·7	1032·0	612·3
20·40	256·86	571·13	314·27	28·40	424·3	1045·6	621·3
20·60	260·59	581·08	320·49	28·60	428·9	1059·4	630·5
20·80	264·64	591·94	327·30	28·80	433·5	1073·2	639·7
21·00	268·26	601·66	333·40	29·00	438·1	1087·0	648·9
21·20	272·35	612·67	340·32	29·20	442·8	1101·0	658·2
21·40	275·99	622·52	346·53	29·40	446·9	1113·5	666·6
21·60	280·10	633·67	353·57	29·60	451·6	1127·6	676·0
21·80	284·22	644·89	360·67	29·80	456·2	1141·8	685·6
22·00	287·90	654·94	367·04	30·0	460·9	1156·0	695·1
22·20	292·05	666·30	374·25	30·5	472·8	1192·0	719·2
22·40	296·22	677·75	381·53	31·0	484·1	1226·8	742·7
22·60	299·96	687·98	388·02	31·5	496·1	1263·7	767·6
22·80	304·13	699·57	395·44	32·0	508·2	1301·1	792·9
23·00	308·34	711·24	402·90	32·5	520·4	1338·9	818·5
23·20	312·09	721·67	409·58	33·0	532·6	1377·2	844·6
23·40	316·32	733·47	417·15	33·5	544·9	1416·0	871·1
23·60	320·57	745·35	424·78	34·0	557·3	1455·3	898·0
23·80	324·36	755·98	431·62	34·5	569·9	1495·0	925·1

TABLE V—*continued*

Kinematic viscosity at 210° F., centistokes	*H*	*L*	*D* (*L*—*H*)	Kinematic viscosity at 210° F., centistokes	*H*	*L*	*D* (*L*—*H*)
35·0	582·4	1535·2	952·8	55·0	1173·7	3582·0	2408·3
35·5	595·8	1577·7	981·9	55·5	1190·5	3643·6	2453·1
36·0	608·5	1618·9	1010·4	56·0	1207·2	3705·2	2498·0
36·5	621·4	1660·6	1039·2	56·5	1224·2	3767·8	2543·6
37·0	634·3	1702·7	1068·4	57·0	1241·1	3830·4	2589·3
37·5	647·4	1745·3	1097·9	57·5	1258·6	3895·4	2636·8
38·0	660·5	1788·3	1127·8	58·0	1276·1	3960·4	2684·3
38·5	674·4	1833·9	1159·5	58·5	1293·5	4025·0	2731·5
39·0	687·7	1877·9	1190·2	59·0	1310·8	4089·6	2778·8
39·5	701·1	1922·4	1221·3	59·5	1328·3	4155·2	2826·9
40·0	714·6	1967·4	1252·8	60·0	1345·8	4220·7	2874·9
40·5	728·3	2013·1	1284·8	60·5	1363·9	4288·8	2924·9
41·0	741·9	2058·7	1316·8	61·0	1382·0	4356·8	2974·8
41·5	756·1	2106·4	1350·3	61·5	1399·9	4424·4	3024·5
42·0	770·2	215·41	1383·9	62·0	1417·7	4492·0	3074·3
42·5	784·2	2201·7	1417·5	62·5	1435·8	4560·6	3124·8
43·0	798·2	2249·3	1451·1	63·0	1453·9	4629·1	3175·2
43·5	812·7	2299·0	1486·3	63·5	1472·6	4700·2	3227·6
44·0	827·2	2348·6	1521·4	64·0	1491·2	4771·3	3280·1
44·5	842·2	2400·4	1558·2	64·5	1509·7	4841·9	3332·2
45·0	857·2	2452·1	1594·9	65·0	1528·1	4912·4	3384·3
45·5	872·1	2503·8	1631·7	65·5	1546·8	4984·0	3437·2
46·0	886·9	2555·4	1668·5	66·0	1565·4	5055·5	3490·1
46·5	902·0	2608·1	1706·1	66·5	1584·7	5129·7	3545·0
47·0	917·1	2660·7	1743·6	67·0	1603·9	5203·8	3599·9
47·5	932·7	2715·5	1782·8	67·5	1622·9	5277·4	3654·5
48·0	948·2	2770·3	1822·1	68·0	1641·9	5350·9	3709·0
48·5	963·7	2825·0	1861·3	68·5	1661·1	5425·5	3764·4
49·0	979·1	2879·6	1900·5	69·0	1680·3	5500·0	3819·7
49·5	994·8	2935·2	1940·4	69 5	1700·1	5577·2	3877·1
50·0	1010·4	2990·8	1980·4	70·0	1719·9	5654·4	3934·5
50·5	1026·2	3047·4	2021·2	70·5	1739·5	5731·0	3991·5
51·0	1042·0	3104·0	2062·0	71·0	1759·1	5807·5	4048·4
51·5	1058·4	3162·9	2104·5	71·5	1779·3	5886·8	4107·5
52·0	1074·7	3221·8	2147·1	72·0	1799·5	5966·0	4166·5
52·5	1090·9	3280·4	2189·5	72·5	1819·5	6044·6	4225·1
53·0	1107·1	3339·0	2231·9	73·0	1839·4	6123·1	4283·7
53·5	1123·9	3399·9	2276·0	73·5	1860·0	6205·4	4344·4
54·0	1140·6	3460·8	2320·2	74·0	1880·6	6285·6	4405·0
54·5	1157·2	3521·4	2364·2	74·5	1901·0	6366·2	4465·2
				75·0	1921·3	6446·7	4525·4

the conversions on graph paper other results can be obtained. Converted results must be regarded as approximate.

It is probably better to utilise the equations which have been worked out for conversion to kinematic viscosity.

Saybolt Universal — A.S.T.M. equation
$\nu = 0{\cdot}00226T - 1{\cdot}95/T$ for Saybolt time less than 100 seconds
$\nu = 0{\cdot}00220T - 1{\cdot}35/T$ „ „ greater than 100 seconds
Saybolt Furol — Garner and Kelly equation
$\nu = 0{\cdot}0224T - 1{\cdot}84/T$ from 25 to 40 seconds
$\nu = 0{\cdot}0216T - 0{\cdot}6/T$ above 40 seconds
Redwood No. 1 — Garner and Kelly equation
$\nu = 0{\cdot}00260T - 1{\cdot}79/T$ from 34 to 100 seconds
$\nu = 0{\cdot}00247T - 0{\cdot}5/T$ above 100 seconds
Redwood No. 2 — Garner and Kelly equation
$\nu = 0{\cdot}02458T - 1{\cdot}0/T$ from 32·5 to 90 seconds
$\nu = 0{\cdot}02447T$ above 90 seconds
Engler
$\nu = 0{\cdot}08 \times E^\circ - 0{\cdot}0864/E^\circ$ for E° 1·35 to 3·2
$\nu = 0{\cdot}076 \times E^\circ - 0{\cdot}04/E^\circ$ for E° above 3·2

CHAPTER X

MECHANICAL TESTING

In spite of all the efforts which have been made to prepare foolproof specifications for lubricating oils satisfaction has not been attained. Such physical properties as viscosity, specific gravity, etc., when used in conjunction with oxidation, carbon residue and other chemical tests can only be regarded as "objective" properties. All these tests are useful and necessary, but they do not furnish all the requisite data to reach a finite conclusion upon the suitability of an oil for a specific purpose. An engine or a machine works under manifold operating conditions, some of which are well known and understood, but others are less known and difficult to investigate, so difficult that they cannot be reproduced on a laboratory scale. Mechanical testing has therefore been widely introduced to implement chemical and physical testing, and must be regarded as an essential part of laboratory routine. Full-scale engine tests are often very expensive and lengthy, and too important to be undertaken until unmistakable signs of success are assured. Sometimes a risk must be taken, but if it fails somebody must bear the cost. The full extent of the risk cannot be foreseen when a heavy metal structure gathering momentum is suddenly deflected from its course by a bearing failure or a seizure of a controlling part. Those who tread into the unknown with the full measure of their responsibility must be sufficiently experienced to navigate if a storm arises. Imagine what could happen if a giant flywheel became unsteady, or a monster turbine rotor started to vibrate, or even a lubricating oil decomposing rapidly in an explosive filled torpedo. Amongst the myriad of moving parts in this world the hazards must extend from zero upwards, consequently it must be left to the individuals concerned whether a full-scale test shall be made.

PETROL ENGINES

Mechanical testing can sometimes be made upon a full size part of a composite mechanism. Single cylinder aero engines are commonplace units to study cylinder wear, piston design and suitability of lubricating oil, or the effect of an oil on bearings under power. Even a test like this is costly, but hundreds of pounds cheaper than a full-scale test. Individual bearings can be assembled in a crankshaft and loaded with a dummy piston whose weight can be varied to increase the load. Alternatively a bearing may be housed in a structure to study it in detail, and to make measurements which could not be made in any other way. Ball and roller bearings are invariably run in a rig to enable temperature rise to be determined with different lubricants under different loads and temperatures. At the conclusion of the tests the bearings are easily dismantled, measured, and any signs of corrosion observed. Small machines can often be utilised without much modification. High-speed sewing-machines are sufficiently small to install in a laboratory where operating power can be accurately calibrated, and the amount of oil spray seen.

Abbreviated researches have been much criticised in the past as not being commensurable with full-scale conditions. Possibly the criticisms were, and still are, justified, but what matters is, something had to be done to make progress. So why be sensitive to too much mental sanity which often clips the imagination of its wings. Diminutive models were made and used mainly because there was insufficient money available for anything different. These models allowed angularities to be smoothed off; many obscurities to disappear, and a more materialistic attitude is now shed upon them. The 250 or 500-c.c. air-cooled petrol engine became a popular type of engine for internal engine lubrication research. The results secured were so encouraging that the tiny Lauson engine was hailed with enthusiasm, but now abandoned. When the abbreviated test results have been obtained larger-scale tests are justified. This is how research upon internal combustion engine lubrication is carried on.

A small J.A.P. air-cooled petrol engine makes a very useful research unit. The temperature can be adjusted and maintained by a regulated air flow, and its power can be absorbed quite cheaply with a Walker air brake. An oil can be tested in the course of hours. Naturally it is not quite so simple as it might appear. A rigid bed is the first requisite to ensure complete stability against the vibrations of a single cylinder engine. Probably the most important part of the test is the fitting of the piston rings. Some preliminary work is necessary to ascertain the correct clearances for the test to be undertaken. The gap clearance controls the fit against the cylinder wall, and the side clearance in the grooves governs the metering of the oil. Another useful air-cooled engine is the Norton sports model. For experiments on a water-cooled engine it is convenient to install a 12 or 14 horse-power model attached to a Heenan and Froude water dynamometer. With an engine of this kind it is possible to remove the sump, and replace it with an oil reservoir standing on scales so that the oil consumption can be measured at will.

Practical research on lubricating oils carried out by engine testing appears to be an uncharted sea, and operations are further handicapped by the fact that nearly all text-books on engine design and testing concern themselves almost entirely with factors relating to the engine itself. Lubrication systems are mainly treated from this standpoint, and lubricants and the testing of lubricants in engines are practically ignored. Experimenters must therefore devise their own conditions of test according to the goal they have in view, bearing in mind that apparent trivial differences in the condition of the test engine, and external factors, often exert a greater effect on results than differences in the lubricant under test. Although every effort may be made to keep conditions constant a number of factors cannot be controlled, amongst which may be mentioned atmospheric conditions. It is often stated that engine tests are so uncontrollable that they are of little value. Such a belief is unfortunate, and if it persists little progress can be expected. Whilst it might be true that these tests were necessarily mechanical in nature, and were not suitable to attract talent, and could only be regarded as intelligence tests, things have changed. To-day it is left very largely to the talented ones to undertake this work, because of the necessity for imagination and skilful fitting of the test unit, and powers of observation.

After a testing unit has been designed and assembled, preliminary tests must be made under various conditions to ascertain its general behaviour, susceptibility to variations, repeatability, etc. Probably the principle aims of the test are to determine oil consumption, carbon formation, cylinder and piston ring wear, and change in the lubricant. It is not primarily to demonstrate performance for a sales campaign. If it were the engine could be suitably adjusted for any specific objective. A test should be undertaken for scientific evidence, and not to convince non-scientific minds. If this truth is followed engine tests will be of inestimable value. As carbon formation is of great importance it is useless to operate an engine under conditions which preclude its formation. A very cool or a very hot engine may produce little carbon, because in the one case it may not form, or in the other it is burnt off. Therefore it may well be considered valuable to determine the engine temperature at which the maximum amount of carbon will form, and maintain this temperature in subsequent runs in order to observe the carbon forming susceptibilities of different oils. A temperature survey of an oil-cooled engine can be made by a pyrometer made of two separate sharpened wires held closely together in small punch marks on the metal surface. For convenience a thermocouple can be embedded in a ring between the sparking plug and the engine. By this arrangement a continuous reading is possible.

Oil consumption is affected by piston ring clearances, engine speed, viscosity, and composition of the oil. From observations on piston rings, in a J.A.P. engine, with varying amounts of wear, it appears that the clearance at the ring gap exerts little influence between ten and twelve thousandths of an inch. This doubtless is due to the carbon formation in the gap and compensates for anything up to very excessive clearance. The side clearance of the rings in their grooves is much more important, consequently the maker's recommendations should be rigidly observed. It was found that by increasing the side clearance from two to four thousandths the oil consumption was doubled. This extra space allowed the rings to move up and down, and thereby pump more oil through. Although carbon does form on the sides of the rings it does not seem to have any material compensating effect on the clearance.

As would be expected, oil consumption increases rapidly with increase in speed. Naturally any increase in speed implies an increase in engine temperature, which must play an important part owing to increased evaporation of the oil. Supporting evidence for this is that the oil consumption curve is steeper than the petrol consumption curve over the same speed range. Petrol consumption is dependent upon speed alone and not on temperature.

The effect of viscosity on oil consumption should be considered in conjunction with the composition of the oil. Clearly viscosity must play a very important role. To illustrate the effect of different blends two oils were made having a viscosity of 240 seconds (Redwood) at 140°F.; one was made from a thin spindle oil and bright stock, and the other a medium engine oil and bright stock. During the first hour in the engine the oil consumption of the spindle oil blend was high, but thereafter it decreased rapidly. At first the spindle oil evaporated rapidly, and as its concentration diminished, and the concentration of the viscous bright stock concentrated the oil consumption decreased. This increase in viscosity would be a disadvantage in practice. The blend containing the engine oil gave

In this case the results are different. The advantage of a thin oil is only experienced at low speeds. At high speeds the maximum output can only be attained when the viscosity is above a definite minimum. Above a certain viscosity the output falls through fluid friction. For this type of engine it is true to say that the viscosity of the oil should not be below a specified minimum.

Tests made on the water-cooled engine do not indicate the oil consumption, but with the air-cooled engine evidence is given to prove that with the proper oils the consumption is at its best. By using a low viscosity oil in a water-cooled engine a saving of petrol can be effected as one would expect from the results already given. Interesting details of this subject are shown in the table giving fuel consumptions when using various oils. The curve corroborates the expectation. But is the economy of petrol the full financial gain? Against it must be placed the oil consumption. A simple calculation will show that the money saved through diminished petrol consumption is eaten up by the cost of the oil consumed. (Fig. 32.)

Therefore all the influences must be taken into consideration when deciding upon the viscosity of an oil to use.

Consideration has been given to starting and running conditions, so a word might well be given to the intermediate or warming-up condition. The curve starts with an oil temperature of 70° F., but from the shape of the curve it is reasonable to suppose that it can be extended in the same general direction. A steady but slow increase in power accumulates during the warming-up until a viscosity is reached at which a sharp break in the curve occurs. These results were obtained on the 12 horse-power water-cooled engine at part throttle to give normal driving load, which at 2,200 r.p.m. was equivalent to 35 m.p.h. From these results it follows that an engine whose oil never warms up to the temperature at which the engine gathers power can with advantage use a thinner oil to get extra power and saving of petrol. (Fig. 33.)

BEARINGS

A vast amount of work has been done on bearings, and the results are scattered widely throughout the scientific literature in the civilised world. Some of it is of a very high academic value. One of the most beautiful summaries on journal and thrust bearings was made by Professor Swift at the General Discussion on Lubrication (I.M.E., 1937). He spoke first of the experimental work done by Beauchamp Tower in 1883 and the classic work of Osborne Reynolds

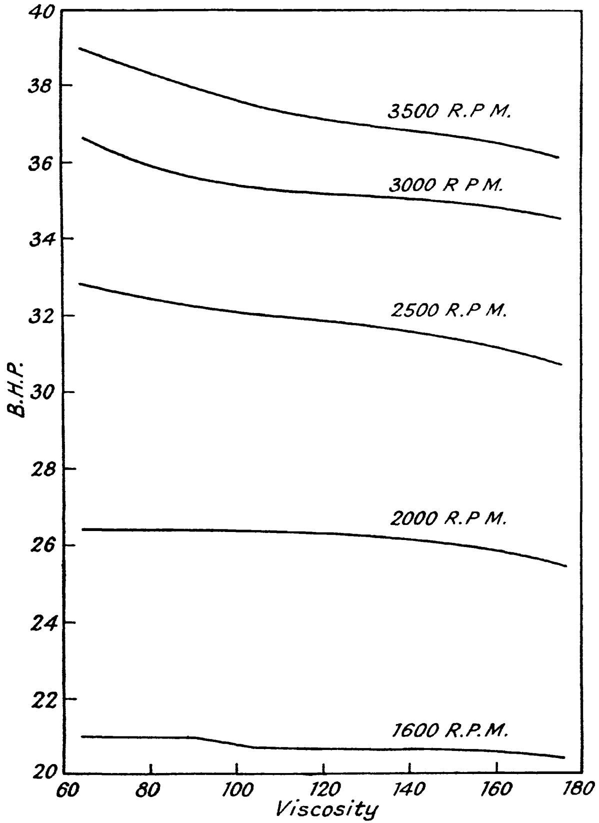


Fig. 30.—Effect of viscosity on Power.
Tests on a water-cooled engine.

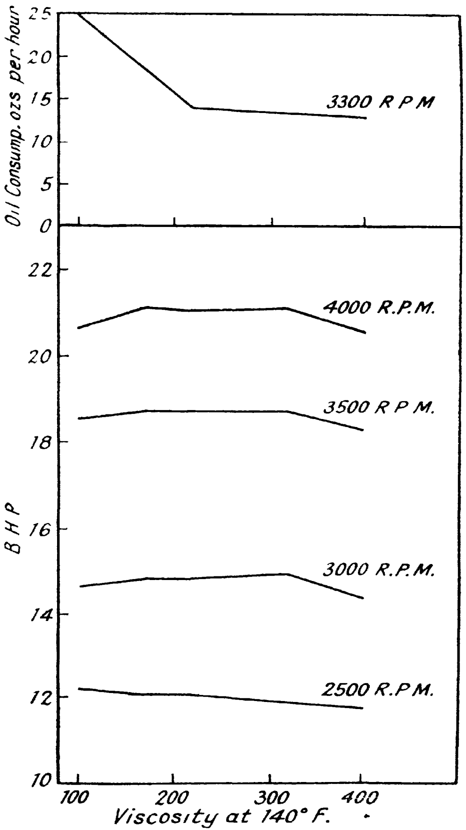


Fig. 31.—Tests with air-cooled engine.

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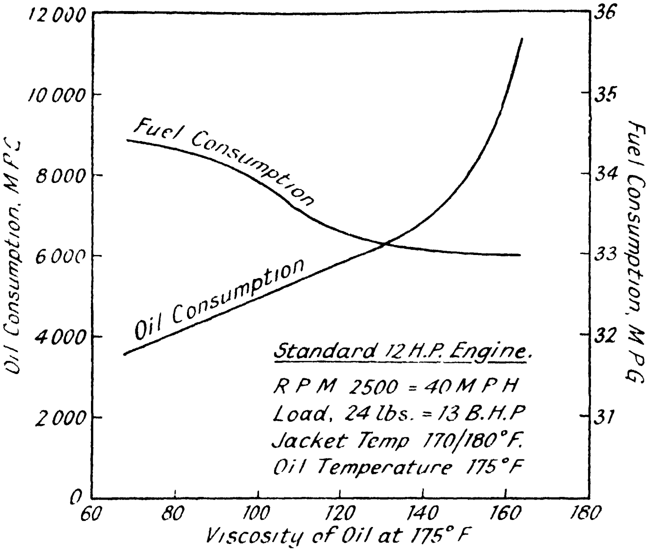


Fig. 32.—Test curve. Fuel and oil consumption. Air-cooled engine.

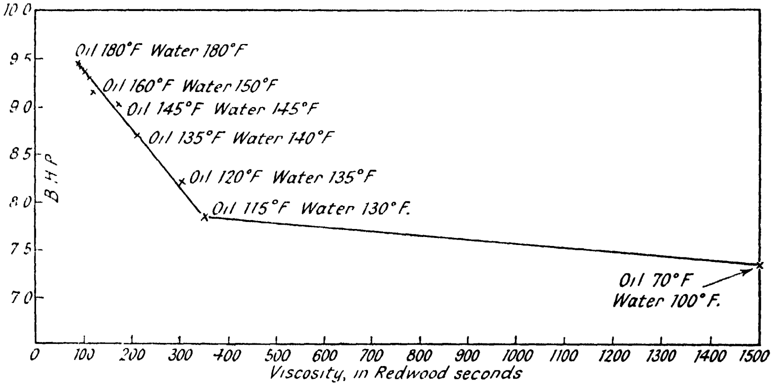


Fig. 33.—Variation of power with viscosity. 12 h.p. water-cooled engine.

in 1886. It was Reynolds who enunciated the principles of the oil pressure film within the bearing which has done so much to make the needs of present-day lubrication possible. Later the problem of the plane thrust pad was so completely solved by Michell that his theory forms the quantitative basis of the design of thrust bearings to this day. The ingenuity of Goodman and Thomson in this country, together with Swift, and Hanocq in Belgium, will long be associated with bearings. On the experimental side of the problem of bearing lubrication, the intrinsic difficulties of technique have taxed the skill of many workers. Following an appreciation of the importance of infinitesimals and an improvement in the precision of manufacture and measurement progress has been rapid. The chief purpose of systematic experiment has been to ascertain to what extent theory is capable of predicting the performance of a bearing, and to provide data useful to the designer. Theory and experiment have now been brought into sufficient agreement to inspire fair confidence in each.

Finality has not yet been reached. New developments in engineering are ever under way. The new conditions imposed keep research in a continuous state of activity. It is only necessary to look at the large number of papers contributed to the General Discussion to realise the magnitude of mechanical testing in the study of bearing lubrication. The general principles of bearing lubrication mentioned in other parts of this book are probably sufficient to indicate procedures to follow. Even though this may be done the work will sooner or later be involved in bearing metals, bonding, alignment, clearances, and temperature.

Often the failure of a bearing is ascribed to the lubricant without pausing to consider other possible causes. That good bonding of the bearing metal to the supporting metal is generally assumed; that alignment is satisfactory, and clearance is correct. All three may be wrong. A crankshaft that is worn and reground has a reduced diameter, the new bearing metal must be thicker, consequently it may be that the mechanic who does the remetalling does not re-tin correctly, or does not re-grind with accuracy, or allows too much clearance. Bad alignment throws too great a load on part of the bearing. Too much clearance permits a rapid succession of hammer blows on the soft bearing metal, resulting in a still further clearance. The part of the bearing which has not bonded is free to move, especially under these abnormal conditions. and finally breaks away.

Tin base bearing metals have a long history of successful usage. but in recent years they appear to have failed in their purpose. The reason is easily explained. Where the loading on the bearings is very severe trouble has arisen due to cracking after limited periods of service. Clearly there is a limit to the endurance of all metals, bearing metals included. The endurance of most metals is closely related to fatigue. Fatigue tests are usually made by flexing the metal at high speed until it breaks. To do this with a bearing would be a bit difficult, but of course it can be done, and is done frequently with a bearing fitted in an engine. A pulsating load in an internal combustion engine must flex the bearing within very narrow limits at high speeds. Sooner or later the bearing metal will develop fatigue cracks, and ultimately fracture. How long this will take depends upon the rigidity of the backing metal, bonding, loading and temperature. Of these, probably temperature is the most common. It is well known that cracking will start during continuous running when the temperature of the white metal keeps at a fairly constant high value. During starting and initial running before the bearing has warmed up, the tensile stresses will be high, but diminish when the bearing is warm. Tensile stresses due to thermal contraction may have an important effect upon the life of a bearing under intermittent running.

To meet high temperature effects copper-lead bearings were introduced. These bearings are different from phosphor-bronze. Copper-lead is primarily not an alloy, but a dispersion of lead particles in copper. The copper may be alloyed with tin or other metal to modify its characteristics, but it is not a lead bronze. Many difficulties have been encountered when using this bearing metal, but they are gradually being explained and remedied. At first they caused excessive shaft wear until it was realised that a hard shaft was necessary. Pitting was ascribed to free fatty acid in the lubricant. Even to-day this assumption has advocates. Unfortunately there is evidence against it. If there is a hazard there would be little sense in using deliberately an acid oil. The trouble seems to appear at temperatures above 150°C. To overcome it a very thin film of indium has been superimposed, but it has not been universally adopted. Some alleviation has been secured by the use of chemical additives in the oil.

Metals intermediate between tin-base and copper-lead, such as cadmium-nickel, have been introduced. They, too, have pitting potentialities, which have been kept in bounds by the addition of tributyl phosphite to the oil. Silver alloys and aluminium alloys have received much study on testing rigs, and have passed to engine testing units.

GEARS

Mechanical testing for gear lubrication has presented many difficulties, and still continues to do so. The makers of gears publish recommended lubricants for specific gears and uses, based largely upon mechanical testing and full-scale observations. This, however, does not exclude further experimental work. The general principle involved in most gear-testing units is what is called the four-square rig. In its simplest form it consists of a driven gear attached by a shaft to another gear, which in its turn operates a gear placed at the opposite angle of a rectangle. The remaining power is transmitted by a shaft to a gear situated at the fourth right angle. The load is applied by imposing a torque on the second shaft. By circulating the input power in this way it is only necessary to install a motor large enough to supply the loss of power due to friction. A small motor is sufficiently large to drive a gear of much greater magnitude. In practice the respective gears can be pinions in mesh, or separate gear-boxes of any design. Power losses by friction efficiencies, temperature rise, suitability of lubricants, and gear wear can be measured.

Hypoid gears present difficulties which have been fought in other ways. Originally full-scale testing was tried, but had to be abandoned mainly on account of high costs. A variety of test machines were introduced ostensibly to measure film strength. Among them may be mentioned the Timken, Almen, Floyd, and Four-ball.

In the *Timken tester* a carefully polished steel block, with a cross-section of 12·5 × 12·5 mm. and 19 mm. long, is pressed against a steel ring, 12·5 mm. wide and 49 mm. diameter, revolving at 800 r.p.m. The load can be adjusted at will. The lubricant is fed at any predetermined temperature to the rubbing surfaces. At the end of the test the width of the scar mark is observed.

The *Almen Machine* has been extensively used by the author for a period of years, and the results given in his publications are largely based upon it. It has been a useful tool for assessing the breakdown value of an oil film containing chemical additives. Whether the results correlate accurately with gear tests is of secondary importance provided it is clearly understood what is in view.

The simplicity of the machine enhances its attractiveness. It consists of a steel rod of 0·25 in diameter, which rotates at 600 r.p.m. in two steel half-bearings. The rod and bearings are immersed in a lubricant contained in a small bath. Pressure is applied to the bearings by successive additions of weights. Each weight places 1,000 lb. per sq. inch upon the bearing. The machine is designed to take loads up to 15,000 lb. per sq. inch. The rod is rotated until a seizure in the bearing occurs when the pressure is increased. Invariably no difficulty is experienced in detecting a seizure because either the driving belt comes off or the rod shears.

All pure mineral oils fail at about 4,000 lb. per sq. in. The film rupture strength of fatty oils is as follows:

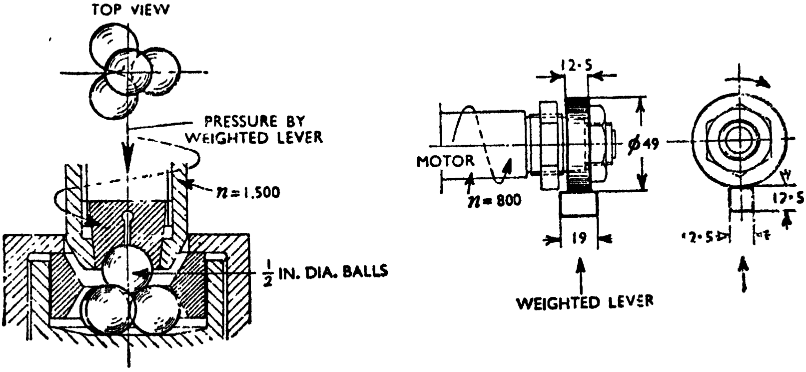
Castor	9,000
Coconut	8,000
Lard	9,000
Neatsfoot	11,000
Olive	9,000
Rape	15,000
Wool grease	15,000

Floyd tester. A steel shaft revolves in two half-bushes of steel. The top bush is loaded hydraulically. Normally the test is carried out at room temperature and the load on the bush is increased every 10 seconds by 25 lb. up to 200 lb., after which the machine has to run under this pressure for 5 minutes. The test is then repeated at 200°F. This time the load is increased in the same way to 325 lb., under which load the machine has again to run for 5 minutes. No other measurements are made. The criterion is that the brass shearing pin that transmits the motive power shall not break. With this tester the specific bearing load remains the same all through the test, at 1,757 kg. per sq. cm. for the applied load of 325 lb.

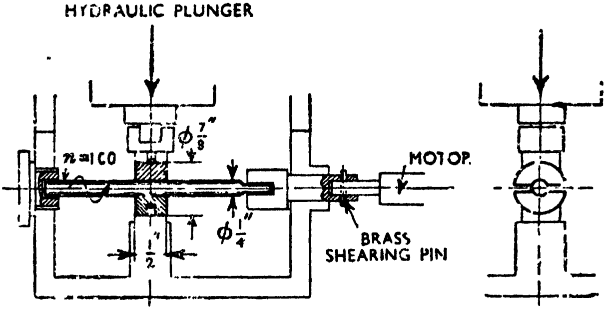
Four-ball apparatus has three half-inch steel balls securely clamped in an oil bath, and a fourth ball placed on top which is free to revolve. Pressure is applied to the top ball, and revolved at 1,500 r.p.m. At first the friction rises, then remains stationary, and finally if the applied load is high enough seizure occurs. The point at which seizure occurs is called the breakdown load.

These several machines do not evaluate lubricants even in the same order, consequently it is difficult to correlate results. Much has been said in favour of them individually. Of course there is no reason why any one of them should not be used for research purposes, or for private reasons. Little purpose would be served here by reviving their respective merits as the machine adopted by the

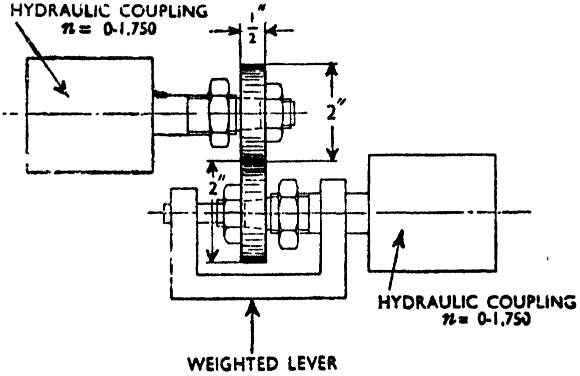
Society of Automotive Engineers in the U.S.A. has superseded all of them for assessing hypoid lubricants.



(a) Four-Ball Tester (b) Timken Tester



(c) Floyd Tester



(d) S.A.G. Tester

Fig. 34.

S.A.E. machine. Two ring-shaped test pieces, 1·91 inch in diameter, half-inch wide, and having conical interior surfaces, are fitted to two revolving shafts, and rotated through suitable gearing. The two rings roll over each other at different speeds under a gradually increasing load. The lower ring is partially immersed in an oil bath. When the oil film breaks down there is an immediate evolution of oil vapour, and a sudden increase in noise.

When making mechanical tests immaculate attention must be given to the rubbing surfaces. Many criticisms of the past were born due to an insufficient appreciation of this one factor. It is exceedingly difficult to define a surface, so it is common to secure a surface by stipulating how it shall be ground or polished, added to which some guidance is usually given about the running-in. With all the care possible erratic results occur, therefore it is necessary to make sufficient tests to ensure that true results are obtained.

Lately considerable attention has been given to the gear-testing unit designed and improved at the Research Laboratory of the Institution of Automobile Engineers. It is of the four-square principle in which the power is circulated directly through the gear wheels. This instrument is useful for studying gear teeth design, materials of construction, wear, and gear lubricants.

Friction Testing

Oiliness machines have not won popularity. Many years ago Thurston designed a machine which for some years had an appeal, and therefore acquired some publicity, but it is never used now. About twenty years ago Deeley did much to popularise his machine, but not very successfully. Most of the work which has been done on the coefficient of friction has been done by research methods with little idea of standardising them for routine procedure.

Miscellaneous Tests

Much valuable work can be conducted by specially made set-ups for detailed examination. Sometimes hastily thrown together bits and pieces will give sufficient information for a particular problem, other times an accurately made, though essentially simple, assembly will provide results of far-reaching importance. It is a mistake to believe that costly and intricate mechanical devices are essential to useful laboratory work. Before embarking upon an expensive programme much time and money can be saved by a preliminary survey with modest materials and a keen power of observation. The more complex a machine becomes the greater must be the precision of its parts if the whole is to run without a hitch.

CHAPTER XI

MISCELLANEOUS PROPERTIES

This chapter makes no greater claim than to record miscellaneous data which may be difficult to find at a moment's notice. In collating such data no references are given, because they have been obtained over a period of years and their origin is not known in every case. Perhaps some of the figures have since been revised, so they can only be accepted as reasonably accurate guides.

	Specific Heat at 20° C.	Surface Tension Dynes per cm. at 12° C.	Dielectric Constant C.G.S. units
Castor	0·508	37·6	4·62
Rape	0·488	36·6	3·06
Neatsfoot	0·483	38·3	3·10
Sperm	0·493	38·3	3·05
Bright Stock	0·476	36·7	2·25
Californian Viscous	0·423	38·5	2·76
Medium Machine	0·460	36·1	2·32

Compressibility of oils can be determined by measuring the supersonic wave velocity. In general, the compressibility of fatty oils is about 10 per cent less than mineral oils. As the product of the surface tension and the coefficient of compressibility of a liquid is almost constant, at a given temperature, the compressibility of an oil can be estimated approximately by measuring its surface tension.

	Surface Tension	Compressibility x 10^{-6}	Surface Tension x Compressibility
Cod Liver	33·2	60·9	2020
Cottonseed	33·5	60·9	2040
Olive	32·9	59·8	1970
Rape	33·6	60·9	2050
Ice Machine	30·7	67·4	2070
Liquid Paraffin	31·5	64·4	2030
Transformer	31·4	65·0	2040

Some oils will show a tendency to solidify under a pressure of 1,000 kg. per sq. cm. which becomes accentuated with time. This may be due to a separation of wax.

According to the International Tables the mean coefficient of compressibility between P_1 and P_2 is defined by the equation

$$\beta = \frac{Vp_1 - Vp_2}{Vp_1\,(P_2 - P_1)}$$

$\text{kg}\ \frac{P}{\text{cm}^{-2}}$	Castor	Rape	Sperm
157	50·5	55·7	60·8
1417	39·4	42·7	45·7

These results are recorded to indicate the change of compressibility under pressure. Another set of compressibility results, in other units, do not harmonise with the previous table, but they are given in case they may be useful.

Pressure Tons	Water	Castor	Sperm	Mineral
1	347000	291000	242000	287000
2	339000	302000	252000	291000
3	—	330000	285000	315000

The thermal conductivity of mineral oils does not vary to any appreciable extent. Fatty oils have a slightly higher value than mineral oils.

	Cals. per sq. cm. per sec. for 1°C. and 1 cm. thick
Castor	0·00043
Linseed	42
Olive	40
Rape	41
Mineral	30
Liquid Paraffin	29
Transformer	27

The refractive index is of value in assisting in the establishment of the purity of some fatty oils, but it has little application with mineral lubricating oils. It has been suggested as an aid to determining the carcinogenicity of spindle oils. So far it has not been taken very seriously. The function $\frac{n_D - 1}{d}$, where n_D is the refractive index for *D* line (approx. daylight) and *d* is the density both at the same temperature, is approximately constant for all types of mineral oils varying between the extreme limits of 0·53 and 0·61.

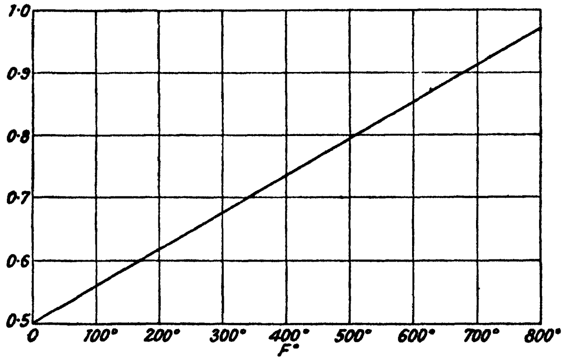


Fig. 35.—Effect of Temperature on Specific Heat.

The specific heat of mineral oils per unit weight is about 0·45, and per unit volume 0·5, at atmospheric temperature. At high temperatures it rises until at about 850° F. it is unity.

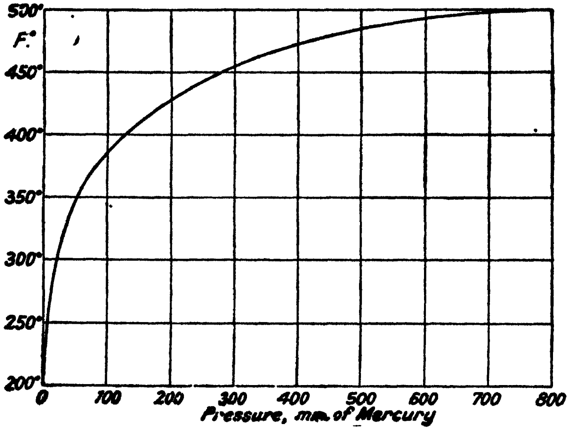


Fig. 36.—Vapour Pressure of Naphthenic Oil.

The vapour pressure of different mineral oils must necessarily vary with the boiling-points of the constituent hydrocarbons. To obtain some indication of how the vapour pressure is affected with temperature a graph is given of a medium naphthenic oil.

The flash point of fatty oils depends upon the free fatty acid content, the method of extraction, and their degree of refinement. The pour point varies with the amount of solid glycerides which have been removed. Neatsfoot, for example, can be prepared with a cold test of about —10° F.

	Sp. Gr.	Flash °F.	Pour Point °F.	Vis. Saybolt	
				210° F.	100° F.
Castor	0·956	550	—15	110	1370
Lard	0·915	550	35	55	206
Neatsfoot	0·916	420	40	50	215
Olive	0·916	450	20	50	215
Peanut	0·917	575	35	—	325
Rape	0·914	540	10	54	260
Rape blown	—	—	15	175	450
,, ,,	—	—	—	200	550
,, ,,	0·960	350	30	300	750
Sperm	0·880	500	30	40	115
Seal	0·926	520	35	—	155
Tallow	0·940	550	40	48	230
Whale	0·920	475	35	28	196

The ignition temperatures of oils in low and high pressure air do not appear to be available, consequently they are given in low and high pressure oxygen.

	1 atmos.	33 atmos.
Sperm	308° C.	140° C.
Lard	273	144
Castor	325	153
Glycerol	412	205
Kerosine	255	175
Spindle	248	178
Turbine	—	253
Mineral A	309	188
,, B	273	187
,, C	286	157

Now that the Ramsbottom Carbon Residue test has superseded the Conradson Coke Residue test in this country comparisons of the two will be useful. To identify the types of oils used other tests are included in the table.

Sp. Gr. at 60° F.	Vis. at 70° F. Redwood	Flash Point	Sludging Value	Carbon Residue	
				Conradson	Ramsbottom
0·858	70	305	1·7	0·01	0·10
0·865	150	300	0·1	0·01	0·02
0·877	120	300	0·6	0·01	0·02
0·899	190	360	0·6	0·01	0·10
0·911	430	400	0·9	0·09	0·17
0·890	420	405	1·2	0·03	0·15
0·920	490	320	1·6	0·07	0·15
0·910	540	375	1·9	0·15	0·26
0·915	700	400	1·4	0·29	0·28
0·930	700	350	1·7	0·15	0·18
0·910	1200	440	3·0	0·31	0·23
0·910	1260	385	0·7	0·06	0·14
0·935	2000	405	2·6	0·16	0·15
	at 140°F.				
0·895	580	500	nil	1·5	1·3
0·895	580	500	nil	0·9	0·7
0·900	600	500	2·3	2·5	2·2
0·910	970	540	2·5	3·5	3·1

The solubility of gases in oils has received some attention, but the results are not widely known. Recently the Research Department of the Institution of Automobile Engineers has been studying the frothing of lubricating oils, particularly in aero engines, and has found it necessary to devote time to the solubility of gases in them. Mills has written a report for private circulation, together with a bibliography. He determined the solubility of air in oil, to Air Ministry Specification D.T.D. 109, at one atmosphere pressure. The average value was 8·4 per cent expressed as volume of air per 100 ml. of oil. At other pressures of course it is different. The solubility of air is approximately proportional to the absolute pressure, and is very little affected by temperature. Carbon dioxide is much more soluble. Rodman and Maude (*Trans. Am. Electrochem. Soc.*, 47, 71, 1925) states that at 25°C. it is 99·1 per cent and at 80°C. 56·6 per cent.

The solubility in water at 25°C. is about

Carbon dioxide	76
Oxygen	28
Nitrogen	1

The solubility of water in mineral oils is sometimes of use to power station engineers when centrifuging turbine oils. At times it is difficult to understand why an oil will emerge from the filter perfectly bright and on cooling becomes turbid. An explanation is that water is much more soluble in hot oil than in cold oil. Another explanation is that the sludge may be soluble in hot oil and less soluble in cold oil.

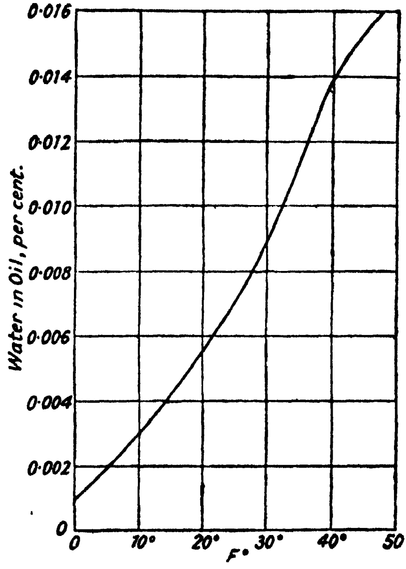


Fig. 37.—Solubility of Water in Oil.

CHAPTER XII

OILS EMPLOYED

To catalogue all the applications for lubricants would be a gigantic task, and unbearable to the reader. A number of typical examples have been chosen to illustrate how oil selection is made. These should enable a reasonable choice to be made by any trained person who is not a specialist in lubrication. The decision may not be the best, but it will probably be safe. Before formulating an opinion, however, it would be well to read all the contents of this chapter to obtain a wider vision of the scheme as a whole. What may appear to be specific to one type of mechanism can often develop ideas which may be of value when considering other branches of engineering.

Aero engines must essentially be classed with other petrol engines, excluding, of course, the few Diesel engines which were introduced for a short time. Their size, power and operational control create differences which isolate them in certain particulars. Their direct association with high power reduction gears, and their comparative lightness of construction introduce separate considerations. Castor oil has been entirely replaced by mineral oil lubricants, and even fatty oil blends have ceased to be used. The last fatty oil to be used was electrically treated rape oil, which was sold under the name of Electrion or Voltol. It ceased with the German occupation of European countries. Whether it will be revived after the war events will show. For many years the British Air Ministry concentrated upon a good mineral oil to specification D.T.D. 109. It was not until 1942 that it was replaced by D.T.D. 472. The major difference between these two oils is that 109 was conventionally refined and 472 is largely solvent refined. Another major consideration is that 109 was accepted upon laboratory acceptance tests, whereas 472 requires an engine acceptance test in addition. In other words, it is considered insufficient to rely upon laboratory tests for the suitability of an oil for aero engines for military purposes. Supplementary engine data are necessary to ascertain their activity on cadmium or other alloy bearings, or their ability to prevent scuffing of aero engine gears.

Oil 109 was designed to accommodate the requirements of British aero engines, but when American-made engines were employed alongside British engines, the subject had to be considered afresh. Furthermore, the territories in which these engines might operate brought into the picture low temperatures on the ground. The result was that three oils of different viscosities were standardised.

	Viscosity at 210° F. Redwood seconds
A	70
B	87
C	107

In normal flight cadmium bearings stand up to the job, but war conditions threw such extra loads and temperatures upon them that it was found that pitting could occur. To obviate this hazard 0·3 per cent, and later 0·5 per cent, of tributyl phosphite was added to the oil. The general idea being that above 160° C. acid in the oil attacked the cadmium. Mercaptobenzothiazole also has an ameliorating effect. It is also useful for copper-lead bearings.

The anti-scuffing chemical compounds have been kept secret.

Oil frothing has given a good deal of anxiety, due to the greater capacity of the suction oil pump over the pressure feed pump. The suction pump obviously must suck air as well as oil. If the aerated oil would part with its air rapidly all would be well. The subject has received a considerable amount of attention, particularly by Giffen at the Institution of Automobile Engineers. So far the only means of dealing with the problem is by mechanical aids.

Piston ring sticking is largely an operational condition which is accentuated in war. Detergents are being tried to prevent it. Of course ring sticking is not peculiar to aero engines. It occurs in any internal combustion engine when the temperature of the ring belt area is exceptionally high.

Ball bearings. Much of the earlier work was done by Stribeck and Hertz for the Ammunition Factory in Berlin. The impetus given to ball-bearing design by Stribeck's findings was followed by the adoption of single-row bearings in automobile work; in fact, it is probably true to say that it was the growth of the automobile industry which gave the fillip to the ball-bearing industry. There was, however, the ever-present fear that balls were unable to carry severe loads on point contact, so attention was paid to rollers. Their main difficulty was in preventing skew, and its consequent increase in friction loss. The subject was investigated by Goodman in 1912. Skewing is controlled by guiding the rollers in a cage or by shoulders on the outer or inner races. Then came the self-alignment bearing to take care of slight deflections in a shaft.

Cages are used to prevent inter-ball friction. In certain cases of high-speed work, particularly where the bearing rotates as a whole and so sets up heavy centrifugal forces, a solid cage is a distinct advantage.

Ball bearings give rolling friction against sliding friction in plain bearings. If the balls were incompressible it would be all rolling friction, but Hertz has shown that compression does occur and the point of contact is expanded into a measurable area over which sliding does occur. Theoretically, oil is the ideal lubricant, but practical considerations impose the extensive use of grease. The finely polished surface of the balls and races are subject to attack by rust through atmospheric action, and may be damaged by the entrance of abrasive matter or other solid material from outside. The exclusion of these entrants can be better obtained by grease than oil. Even breathing of bearings is sufficient to encourage external material to enter. Grease is so widely used that it is probable that grease is used up to as high a speed and temperature as possible, but not for very high temperatures. It is a fatal mistake to over-pack a bearing with grease, because an excess introduces churning friction and therefore heat. To attempt to reduce the temperature of a hot bearing with more grease results in increased heat. Grease is much easier to retain than oil.

Solid lubricants should not be used as they may jam under the balls and cause fracture, particularly with a pre-loaded bearing. A pre-loaded bearing is one which contains an outer race shrunk on to the balls to ensure freedom from clearance between the moving surfaces—very useful for gears, etc. Anything which encourages slip must be avoided, although, of course, there must be some slip between the balls and the races. Rotation occurs about two axes. The spinning effect may be of the order of one revolution in one direction and 600 in another or normal direction. This is an advantage as it ensures a change of surface.

Ball bearings are much more costly than plain bearings, but the friction is much less and is constant practically under all running conditions. This is very important at the moment of starting, when friction is highest. For electrical machinery they are advantageous for maintaining a constant air gap and so maintain the power factor at the maximum. On electric trains they are fitted extensively. For high-speed work, as in woodworking machines, they are almost indispensable, and are lubricated with oil to cut down churning losses.

Lime-soap greases are used for running temperatures up to 120–140° F., soda greases up to 200° F., and oil above.

Bearings. Wood was a satisfactory bearing material as long as there was no need to move loads rapidly, but when war became an established part of national life and a greater mobility thereby necessary, metal-lined bearings were required. When metal bearings came into use is not known, but horse-drawn chariots were employed in the Trojan War, 1100 B.C., and probably by Rameses II in 1300 B.C. After that period little is disclosed about bearings until the Middle Ages, when horse-drawn vehicles with wood bearings were mentioned. It was not until the fifteenth century that any progress was made. The literature seems to indicate that the prototype of the roller bearing was made about 1588. Wood bearings were often lined with iron, brass, bronze, leather or fabric. Alloy bearings were introduced between 1792 and 1817, but not with conspicuous success, because they were soft and were liable to be squeezed out. However, in 1839 Babbitt, in U.S.A., patented the invention of enclosing a soft alloy in a hard shell to prevent the extrusion. In those days lubrication was effected by any fatty oil which was to hand. Olive oil and animal fats were in free supply, and it can therefore be presumed that they were the principal lubricants.

Now bearings are so numerous in size, speed and loading that only generalisations can be made. The method of application and risk of drip are often the controlling factors in the selection of a lubricant. Bearings which are automatically oiled can, in general, use a less viscous oil than those which are hand-oiled. Automatic oiling includes ring feed, drip feed, constant oil-level baths and mechanical lubricators. These forms of lubrication ensure a constant supply during the whole of the working period, whereas hand-oiling is essentially intermittent, and may even approach famine periods. To guard against these periods a more viscous oil is recommended to safeguard the metal against wear and seizure. Factories which are rich in shafting and lightly loaded machines may experience very high peak loads when starting up from cold, even if the oil is slightly too viscous. To remove some of this disadvantage workshop heating regulations have come as a welcome aid. Shock loads must throw heavy loads momentarily upon the bearings, that being so, the viscosity of the oil must be increased to take care of the maximum load. The health of the operatives must also be taken into consideration, hence low viscosity oils which are apt to atomise or vaporise readily and be inhaled should be used with caution.

Temperature effects may modify alarmingly all the preconceived ideas based upon all other factors. To see its effect most clearly it is best to look upon the extremes, very hot and very cold. At these extremes of temperature the viscosity of an oil is profoundly different; in fact, it is often difficult to visualise how viscous a thin oil can be at low temperatures, and how very thin a viscous oil is at high temperatures. In Poland, in the depth of winter, transformer oil has been used for lubricating railway-axle bearings, and light shafting has been lubricated with viscous cylinder oil over furnaces.

These references are sufficient to indicate the many variables which must influence the choice of a bearing oil, and that it is insufficient to follow the old maxim of low viscosity oil for high speeds and low loads and high viscosity oil for slow speeds and high loads.

Bearings on line-shafting do not present serious difficulties as a rule, as most of them are in factories where temperature variations are small, loads reasonably constant and of sufficiently generous dimensions to avoid troubles. There is no specific rule to follow, but a rough guide can be obtained by associating size of shaft with viscosity; e.g. 1 inch with 500 seconds (Redwood) at 70° F., 2 inch with 1,000 seconds and 3 inch with 2,000 seconds. This approximation will need adjustment with individual needs. It is customary to use pure mineral oils on such bearings.

In laundries, and where water is liable to wet the bearings, it is better to use a compounded oil so that an emulsion will form with the water, thereby ensuring a continuous film of lubricant. Should a mineral oil be applied and then water, there is a serious risk of water displacing the oil, and the oil film not being able to recover. The extent of the emulsification necessary need only be slight and temporary, in fact only just sufficient to deal with the small amount of water which can be carried into the bearing at any one moment. Probably 5 or 10 per cent of fatty oil in the lubricant is adequate.

For bearings on reciprocating marine engines it is customary to add 10, 15, or even 20 per cent of fatty oil to guard against film displacement. The fatty oils used are either blown rape or blown fish. Locomotive bearings are commonly lubricated with compound oil, but not so much for the same reason. Rape oil is chosen because of its high film strength. Stern tube bearings on ships use readily emulsifiable lubricants, because they are in constant contact with salt water, consequently the fatty agent employed is wool grease.

High temperatures present many difficulties which need individual solution. Hot roll necks on metal rolling mills are often lubricated by placing raw suet on the hot bearing. As the fat is enclosed in membranes it melts and escapes slowly. A stream of water reduces the temperature of the bearing and prevents the mass of the suet from melting. This primitive system is being superseded by mechanical lubricators feeding steam cylinder oil. There is, however, a limit imposed upon the use of viscous oils by carbonisation at high temperatures. A filtered cylinder oil will often give cleaner working surfaces. Bearings at high temperatures can sometimes be dealt with in a similar manner to chains. In 1930 a change began with roll-neck bearings introducing a circulating lubricant system.

Although greases are outside the province of this book it should be stated that soda-soap greases are widely used for hot bearings.

Bearings which form an integral part of a machine are dealt with in their appropriate place.

Cable oils are not likely to be encountered by readers of this book, except specialists in the subject, nevertheless an introduction may be of interest to users of cables.

The insulation of high-tension cables is composed almost exclusively of paper impregnated with an insulating compound. A single core cable consists of only one copper conductor composed of a number of strands of wire. Of the three conductor cables there are several varieties. The insulation of these cables is effected by wrapping paper tapes helically around the conductors. Then the cable is dried in a steam-heated vacuum tank. Whilst the vacuum is maintained the insulating compound is introduced into the tank in sufficient quantity to immerse the cable. High temperature and low pressure within the tank reduces the viscosity of the compound to enable it to flow easily into the paper wrapping, and de-gasifies it. After the required interval of time for these two actions to occur, the pressure is increased to force the compound into the cable.

Mineral oils are generally used to impregnate the paper. For some high-tension cables a low viscosity oil of the transformer oil variety is used. Usually this type of cable is linked to boxes containing oil which serves to maintain a constant quantity of oil within the cable. Other cables are filled with a viscous compound of filtered cylinder type of oil compounded with resin. In view of the fact that the oil must penetrate the cable with the utmost ease, it is clear that the compound shall have a low viscosity at the temperature of penetration. At atmospheric temperature the compound must be sufficiently viscous not to flow. Hence the compound must have a low viscosity index. The addition of resin lowers the viscosity index. For cables which are permanently supported in long lengths in a vertical position, such as in mine shafts, petroleum jelly is often used. When jelly is used the cable may be partially impregnated with oil before the jelly is applied, to effect a perfect impregnation.

Thermal expansion is an important characteristic. A compound which has a high coefficient of expansion will flow backwards and forwards under temperature changes, thus tending to create voids in the cable insulation. An average of $0{\cdot}8 \times 10^{-3}$ per degree Centigrade, may be considered as representing the expansion of a cable compound between 10° and 60° C. The addition of resin tends to lower slightly the expansion change. The presence of dissolved gases increase the expansion as the temperature rises, consequently the compound must be de-gassed. A method for de-gassifying is to spray the compound on to a rotating disc in a vacuum chamber as it passes to the impregnating tank. The function of the disc is to produce a thin film of oil from which the gas can readily escape. The amount of air which a mineral oil can dissolve is considerable.

An essential to all cable impregnating compounds is the electrical insulating property. Oil is selected because of its high electrical resistivity, which is high at low temperatures, but it diminishes as the temperature increases. Ageing or oxidation also diminishes resistivity. Profiting by this knowledge, it is prudent to select an oil with a low oxidation value, and to exclude air from it after it has been de-gassed. Any oil which is chosen must be generously earth treated immediately before being used, to abstract as far as possible oxidation products. A slight contamination with oxidation products may lead to serious electrical losses from the cable.

Resin increases the viscosity of the oil, and makes it adhere to the paper more effectively, thus checking downward drainage. It also has the advantage of reducing the tendency towards the formation of "cheese," and it stabilises the power factor during the life of the cable. The ordinary resin of commerce is not usually sufficiently clean for cables, therefore it must be cleaned and even refined. The quantity dissolved in the oil is 15 to 20 per cent, or occasionally higher. In addition to viscosity increase, the resin will increase resistivity.

Of the tests which may be applied to cable oils the most important are for resistivity, power factor, viscosity, and wax. Wax formation is not a very accurate description. The compound which is found in cables in use is sometimes called "cheese" or simply X, because its composition is unknown.

Before the cable is inserted into its duct, it is often well served with petroleum jelly to serve as a lubricant, and to arrest corrosion. It is stated that efficient lubrication reduces the pulling tension up to 50 per cent. The pull on the cable is something of the order of 10 lb. per foot run of cable for dry duct and clean lead. A dry duct and lubricated lead will be about 5 lb. The use of soapstone is favoured by some engineers in the U.S.A., who allege that it reduces the friction by 25 to 40 per cent of that of unlubricated lead.

Chains are mainly employed for the conveyance of materials, and for the transmission of power. The conveyance of materials is beset with a variety of conditions, each demanding its own considerations. Should the conveyed material be an abrasive like sand or cement, it may be more economical to run dry and allow wear to take place naturally than to apply a lubricant which will collect and feed abrasive into the moving parts. On the other hand, a thick grease might be applied solely to keep the abrasive from penetrating. A little common sense is usually sufficient to make the decision. A chain passing through a baking oven or a stove enamelling plant is raised to temperatures high enough to make lubrication difficult. If the temperature is not too high to clog the chain with deposit, a steam cylinder oil is effective, but when the temperature is excessive, a medium viscosity straight distillate is useful, particularly if it contains a small quantity of colloidal graphite. The oil is gradually vaporised as the chain passes into the hot zone, but lasts long enough to ensure lubrication. When all the oil has gone a minute film of graphite remains to prevent seizure. The amount of graphite should be kept below 1 per cent. Should the lubricated chain pass into an oven in which there are foodstuffs, care must be exercised to avoid oils likely to flavour them. For very hot chains in glass works, lubrication can be provided with a thin oil frequently fed. The idea of using a thin oil is to ensure that carbonisation is avoided. If chains operate under water, special lubricants are used.

Chains for transmission of power may be open to the atmosphere or encased. The open type may be free to collect all sorts of rubbish, consequently what was stated about abrasives in the preceding paragraph applies also in this case. Grease applied to the outside of the chain is useless, because it cannot penetrate to the rubbing surfaces. It is essential that the lubricant shall be introduced into the bearing of the chain made up of a roller and a bush. Uncovered chains are usually lubricated by immersing them in a bath containing molten petroleum jelly, and then allowing them to drain above the bath whilst still hot. The temperature of the bath should be between 140°F. and 200°. For lighter chains such as bicycle chains, hand oiling is effective, but it is prudent to wipe off excess oil to obviate spraying as the chain travels.

Enclosed chains may be lubricated with oil drip, spray or an oil bath. In selecting a suitable viscosity, consideration should be given to the speed of the chain and the temperature of operation. Coulson (Gen. Dis. 1937) states that the pressures under which the joints operate may be as high as 3,000 lb. per sq. in., calculated on the projected area of the bearing, though specific pressures much lower than this are more general; in fact where the service required from the drivers is continuous, or the application is of a special nature pressures of 1,250 lb. per sq. in. are aimed at. The load on the bearing is intermittent due to the passage of the chain from the driven pinion under load to the driver, and from the driver without load to the driven wheel. Thus a period of quiescence is introduced which allows time for the lubricant to re-arrange itself for its duty. From these facts it becomes evident that oils of too low a viscosity should not be used.

Cutting Fluids are usually scheduled into the three groups, pure mineral oils, compounded oils and soluble oils. The two former are non-emulsifiable, but soluble oils are emulsifiable with water. The function of a cutting fluid is to facilitate metal-cutting operations.

Metal cutting or turning is different from the popular conception of cutting. Research which was done nearly twenty years ago at the National Physical Laboratory showed that a cutting tool acts more like a wedge than a knife, thereby splitting off the shaving from the metal. The cutting tool is so designed to force the metal to split according to desire. This is accomplished by grinding the cutting tool to certain well-defined angles. The point of the cutting tool exerts a shearing force and a crushing force. When the metal is brittle it disintegrates into small chips, but if it is not brittle a shaving curls over the tool. As the shaving curls away a crack develops in the metal and leaves a cavity just above the cutting point of the tool. The tool burnishes the cut surface as it moves forward due to the high pressure between the two surfaces. The friction of the shaving passing over the tool and the tool passing along the metal gives rise to much heat. The local temperature on either of these surfaces may rise to 1,000° F. The function of the cutting fluid is to reduce it as far as possible. In order that a cutting fluid shall be effective, it must be applied in the proper quantity and in the correct way. A too rapid cooling may, under some conditions, damage the tool by quenching it and so altering its structure.

The first essential qualification of a cutting fluid is to absorb heat during the cutting operation. Oils have only a specific heat of about 0·5, whereas water has a specific heat of 1·0. This means that twice the volume of oil is necessary to absorb the same number of heat units as water. If heat removal were the only consideration, then water would be chosen as the cutting fluid. For some classes of cutting water can be used, but for certain reasons which will be described, water alone is rarely used. Oils have a very definite lubricating power which checks the formation of frictional heat between the chip and the surface of the tool, consequently it may not be so vital to cater for a large abstraction of heat when oil is used. Water is an attractive coolant due to its high specific heat and negligible cost, but the rust which follows its use on ferrous metals militates against it. Washing soda has been tried but without real success. Following these efforts oil-water emulsions came into being. Cutting pastes made from mineral oil, soap and water gained popularity for a time. Although a considerable amount of patience was required to mix them with water, sometimes involving mechanical mixing, they had a good adherence to metal. In a few machine shops they are still used. A well-made paste has good keeping qualities, but cut prices brought into existence emulsions which were susceptible to rancidity, odour development and media for pathogenic organisms. The addition of disinfectants acted as partial

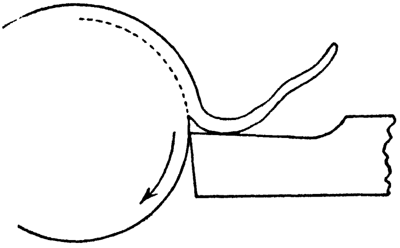


Fig. 38.—Metal Cutting.

correctives. To resort to correctives is not the ideal way of solving the problem. It is better to utilise a product shorn of such disabilities.

Soluble oils made to resemble mineral oils in appearance and fluidity appeared on the market. The pastes were viscous or almost solid emulsions white or pale yellow in colour. The appearance was largely due to the oleine soap from which they were made. By the introduction of resin soap a fluid transparent soluble oil was made possible. A soluble oil when poured into water produces a milky solution at once, even with gentle agitation. Although resin soaps are still used they have been criticised on account of gumming on the moving parts of the lathe. To check gumming sulphonated castor oil was substituted as the emulsifier. Unfortunately castor oil is very costly, therefore alternatives were sought. Sulphonated fish oils soon found a place in soluble oil manufacture, and other competitors were naphthenic acids and petroleum sulphonates Other emulsifying agents are also used. The manufacture of soluble oils is a specialised trade which requires a particular skill to ensure a bright transparent product which will mix with water instantly, and then retain a homogeneous emulsion. It is a mistake to pour the soluble oil on to water and pause before mixing. During the pause some of the emulsifier may be extracted by the water and so upset the emulsibility.

Lately soluble oils made from extreme pressure oils have appeared. They have been found effective for cutting aluminium, aluminium bronze and even hard steels. During war-time when fire risks are considerable, a wide range of non-inflammable cutting fluids is very desirable, consequently it is possible that sulphured soluble oils may have extensive uses.

Now comes the real difficulty of deciding when to employ one type of cutting fluid and when to employ another. In some shops soluble oil is used for drilling, turning, hobbing and broaching. On the other hand, one well-known machine tool maker has a definite policy of recommending a non-emulsifiable oil on machines performing hobbing, gear cutting, and for all automatic and semi-automatic machines. Their argument is that tools are costly, and any slight wear will affect the dimensions and finish of the machined product. The more expensive and intricate the machine and its tools, the greater is the argument in favour of neat oils. A modern turret lathe is much more robust, accurate and costly than its predecessor, so the owner cannot afford to jeopardise it through wear, corrosion and loss of accuracy. Should the driving electric motor be in close proximity to the lathe and likely to be wetted with the cutting fluid, it would be inviting trouble to use a water emulsion.

Magnesium is invariably cut dry owing to the risk of fire. Cast iron is also usually cut dry because the swarf is almost a powder which sticks to everything when it is wet with water or oil, and makes an awful mess. For very high-speed cutting carbide tipped tools are employed. They can resist the effects of heat admirably, therefore they do not normally demand a cutting fluid. Further, if a fluid were used for very high-speed cutting it would be scattered all over the place by centrifugal action. High tensile steels impose severe conditions on the cutting tool, so it is advisable to choose a super-fatted sulphured oil. The expression sulphured oil was introduced by the author to implement the expression sulphurised oils. Normally sulphurised oils are made by heating oil with sulphur until combination is complete, whereas sulphured oil is sulphurised oil which is supersaturated with free sulphur. An advantage of sulphured oil is that it can be used with a very low viscosity, which has the useful property of swilling away the swarf freely from long holes as in gun barrels. Sometimes it is an advantage to add a quantity of organic chlorine addition agents. Whenever a really good finish is required a sulphured or compounded oil is favoured. For aluminium, kerosine is widely employed, though some engineers add a small percentage of fatty oil. When compounded oils are referred to they include mineral oil containing 5, 10 or 25 per cent of fatty oil; the most widely used are those containing 10 per cent, the 25 per cent oil is used on better-class work.

Lard oil was for many years looked upon as having superlative qualities for cutting, but it has disadvantages. In cold weather it is very prone to deposit solid glycerides, and even to solidify completely, and in hot weather it is likely to become rancid. Rape oil is free from these objections. Some people suggest that it will form gummy deposits, but the author has not confirmed this fear.

Without doubt the most widely used coolant is soluble oil, partly because of its cost and partly because of the quantity of metal cut which only requires an emulsion.

The subject of cutting oils cannot be left without a word about dermatitis. This skin affection is a great anxiety in many industries, and a source of much absenteeism. Pages could be written on the subject, and perhaps should be written to reduce the anxiety and to assist in its extermination. Very briefly, the position is that the pores of the skin do not take kindly to any material which ceases them from functioning freely. It matters little whether it be chocolate, soot or dirt. Dry solids can be removed by ordinary washing, dirt which is held in suspension in fatty oil is also easily removed because the fatty oil is emulsified with soap and washed away with water. Mineral oil is different; it is not easily removed by ordinary washing, it demands a special technique. To tell a grown-up man or woman that he or she does not wash properly is inviting an embarrassing moment, but to explain that industrial conditions demand special considerations for personal hygiene is acceptable. The first step to remove mineral oil is to wet the soap and rub it in to the dry skin wherever the oil may be. It is well rubbed in; in fact, massaged into the pores. By this process the soap in a very concentrated state is incorporated into the minute globules of oil. When this has been accomplished, and not before, a little water is applied, and well rubbed in to form an emulsion in the pores. After this operation water can be used more freely, still working the skin to squeeze out the emulsion and dirt. The cleansing effect is spectacular, provided it is done conscientiously, the skin is much improved, and the nails can be cleaned with ease. Warm water is advantageous, but not essential. Gentle scrubbing is allowed, but coarse and hard bristles are to be avoided. By this simple scheme dermatitis has been eliminated from many factories. Should septic sores appear, it is of course necessary to seek medical aid. The author will be pleased to supply prescriptions, which have been successful, to medical men.

Gears are often lubricated with oil which is unnecessarily viscous, due no doubt to the inability of the gear-case to retain a less viscous oil, and perhaps by a continuity of the old idea that they were necessary. Efficient lubrication, however, is only one aspect of gear lubrication. Open gears attached to cement rotary kilns, rolling mills, and the like, do not usually have a high tooth pressure, nor high speed; therefore, theoretically, they could be lubricated with a comparatively thin oil, but practically this is not possible. It is usual to apply a thick adhesive lubricant by hand or other simple means. Bitumen containing lubricants are often used because they adhere well, maintain a thick film, and are not washed off by rain. The method of application has been rendered more positive by diluting the lubricant with a volatile solvent, and feeding it through a mechanical lubricator. This system has wide possibilities, provided a careful choice of solvent is made. Inflammable vapours near to an ignition point would have to be avoided, and the passage of trichlorethylene through a hot zone might readily evolve the poisonous gas phosgene. Should the gears be in an enclosed space trichlorethylene would be a possible danger to life. So should this method of application prove attractive to an experimenter, expert advice should be obtained. Noisy gears and non-precision gears do improve their apparent performance through the use of the more viscous oils. Sometimes it is not convenient or mechanically possible to make a gear-case oil-tight. In such cases it is legitimate to employ a lubricant which will be retained. When this is the case, temperature conditions must be taken into account when it is selected. Gears moving within a narrow band of temperature do not present the difficulties encountered when the temperature range is considerable. Viscous petroleum jellies or oils become steadily thicker as freezing-point is reached and passed, and therefore less able to flow back to the pinions after they have been channelled. As the temperature rises they lose viscosity and perhaps leak from the gear-case. To meet this difficulty lime-soap greases of suitable consistency are chosen. Soda-soap greases would not be the first choice, because they have a lower film strength, and are less easily made to prevent syneresis (oil separation). Aluminium and lead soap greases can be used under certain circumstances.

Motor vehicle transmission gears and their boxes have been so much improved in every way during recent years that fluid lubricants are almost universal. Flow of lubricant from the rear axle to the brake drum was a serious problem to combat until good oil-retaining devices were invented. Now fluid lubricants are used, but not necessarily as fluid as those in the transmission box. The introduction of the epicyclic gear demanded a thin oil, and the synchronous gear was unsatisfactory with viscous oil, therefore there was an incentive for these reasons alone to design an oil-retaining box.

The hypoid back axle brought in a new problem. Its high loading and sliding friction created a demand for lubricants with exceptionally high film strength which could only be met by chemical addition agents. When these new lubricants were introduced, they were described as extreme pressure or E.P. lubricants, but to-day it is insufficient merely to ask for an E.P. oil for a hypoid gear, it is necessary to ask for a hypoid lubricant. Extreme pressure lubricants now cover a very wide field of materials for many purposes.

When it is necessary to use a lubricant of higher viscosity than is normally essential, consideration must be given to the loss of horse-power caused by churning the lubricant. With small-powered gears, the loss may be as much as 50 per cent of the input power. Another factor often overlooked is the necessity to ensure the proper rate of feed of lubricant to ball bearings carrying the shafts. Also to ensure the maintenance of an adequate level of lubricant.

Worm gears are best lubricated with castor oil, but unfortunately it cannot always be used. Castor oil is susceptible to oxidation and polymerisation, particularly at temperatures above 100° C. The chemical change is accelerated by the presence of iron and copper dust, and their soaps. When the oil develops acidity above 2 per cent it may attack the metals and form soaps, which in their turn lead to further acid production. Sometimes the free acidity rises to as much as 12 per cent. Polymerised castor oil may appear to be noticeable merely by increased viscosity, but it may also be as a rubber-like deposit. In spite of these drawbacks and its cost, it is still worthy of consideration when the working temperature of the oil is below 80° C. The second choice of oil would be a good Penna mineral oil having a viscosity below 350 Redwood seconds at 140° F. The reason for this selection is that it maintains the efficiency of the gear at almost a constant up to 60° C., but above this temperature it diminishes. Naphthenic oils allow a steady loss in efficiency as the temperature rises from a little above atmospheric.

Precision gears must be considered individually. They are very carefully designed, and very accurately cut. A few ten-thousandths of an inch tip-relief may have a profound effect upon the life of the gear. Pitting and scuffing of the tooth face must be zealously guarded against. This may not be possible by engineering ability, but by increasing the oiliness and film strength of the lubricant, much can be achieved. Chemical addition agents are now available for this purpose.

Light Mechanisms. The lubrication of light mechanisms of the clockwork type, or the footstep bearing of an electricity meter, or the bearing of an electric clock seems to be so insignificant as to pass unnoticed until attention is suddenly arrested by the information that the bearing pressure may be 75 tons per square inch. How little does the householder who uses electric light realise that in his house is one of the most heavily stressed bearings in existence, and that if it is not lubricated properly he may receive more electrical units than he pays for.

The bearing of the electricity meter consists of a hardened ball-ended steel pivot which rotates in a highly polished sapphire. As the steel pivot has a radius of only 0·025 inch the difficulties of finding the ideal form of lubrication can be imagined. First of all, is lubrication necessary? For a time the bearing runs happily without oil, but if it is to operate for a prolonged period it must be lubricated. If, however, a diamond is used there is much less need for lubrication, whether this is due to the hardness of the diamond or to the structure of the carbon molecule is not known. The major factor which has led meter engineers to seek a suitable lubricant has been the production of ferric oxide from the steel pivot in the jewel cup. This oxide is highly abrasive, so that lubricant used must be capable of holding it in suspension. For this purpose a highly viscous non-oxidising oil is used.

Electric clocks operating off the mains can roughly be divided into two classes: those in which the electrical portion is wholly enclosed and those which are not wholly enclosed. Before attempting to lubricate either, instructions should be obtained from the makers, as it is essential that the correct lubricant shall be used. The makers have had difficulties to encounter, and have been compelled to adopt carefully chosen lubricants.

Lubricants for watches and clocks have only been made by a few firms who have specialised in this class of work. Before the war they were mainly imported from Germany and America, and to a lesser extent from France. The German oil was based upon neatsfoot oil. The neatsfoot oil was subjected to a series of freezing and filtering to remove glycerides which might separate on exposure to cold. Since the war a similar neatsfoot has been made in this country by a similar process, and in addition the free acid is removed. It is then blended with a mineral oil containing an anti-oxidant to reduce gumming. The American oil contains porpoise oil. Some watch oils are white mineral oils, but there is a belief that they are inclined to spread away from the bearings. To guard against spreading, very pure stearic acid in a volatile solvent is sometimes painted around the bearings. Impure stearic acid does not appear to be satisfactory. When a watch requires cleaning it is chiefly due to lack of lubrication. Of course, some dirt may be in the bearings, consequently it is bad practice to remove the movement and immerse it in a solvent to wash out the dirt, as it leaves the bearings quite dry. In this state the spindles will rust and abrade.

Clocks are lubricated with a similar oil, but usually a little more viscous. Mineral oils are used more freely, but ignorant of the fact that they develop acids which attack the brass plates, and the copper soaps produced oxidise the oil.

Fine instruments are in the same category as watches and clocks from the point of view of lubrication. The trigger mechanism of expensive sporting guns are also lubricated with similar oils.

There have been efforts to introduce esters of various types to replace fatty oils, but they have not been well received. Among those which have been tried are tricresylphosphate, valeric and lactic esters.

Petrol Engines are mainly used for transport vehicles. Apart from detail of design they are, in the main, similar except in size and power. The conditions under which the oil lives in these engines is similar though different in intensity. The one foe to oil is oxygen. The ravages of oxygen can be intensified by heat and catalysts. Petrol-engine lubricants must therefore be resistant to oxidation. For this reason oxidation tests have been introduced. How far they have served a useful purpose is a matter of considerable doubt. Moerbeck (Gen. Dis., 1937) attacked them with unrestrained ferocity. Possibly he was right, and his reasons were logical. However much one may agree with him in his arguments, one is forced back to the desirability of having a comparatively simple laboratory test for acceptance purposes. The necessity of engine trials is accepted, but they are long, tedious and expensive. In the development of a lubricant preliminary laboratory work is done, followed by engine bench tests and confirmed by road or track trials. Upon these series of results conclusions are reached, and by no other route can they be obtained yet.

The Conradson carbon test has had many advocates in the U.S.A.; it has, also, had its critics. In this country only a lukewarm enthusiasm has been given to it, and this is not because we have the Ramsbottom coke test. The Air Ministry has introduced for aero-engine oils a coke-cum-oxidation test. The Ramsbottom coke value is determined before and after blowing. A high quality is assumed when the ratio of coke (*a*) to coke (*b*) is low. There is a good deal to be said in favour of this test, but without an engine test it can only be regarded as a signpost. The author has found much assistance from heating the oil in a petri dish in the presence of iron filings, and then determining the petroleum ether insolubles, acidity, and increase in viscosity. The results correlate reasonably well with engine tests.

Of late years there has been a steady flow towards lower viscosity oils. They were demanded by the introduction of self-starters, and have been made possible by better-fitting pistons, rings and bearings. In starting an engine it is important that an ignitable mixture should reach the cylinders as soon as possible, and that there should be a rapid succession of explosions. To effect this there must be a high cranking speed. This can only be accomplished either by a heavy drain on the battery or by using a low-viscosity oil to keep down fluid friction. A few feeble explosions and then a stop repeated several times is almost a sure indication that the engine is not developing sufficient power to overcome its own internal frictional resistance.

Low-viscosity oils may give the impression that high consumption must result. Such, however, is not necessarily the case. Engines fitted with high-pressure rings keep oil consumption within normal bounds. When medium-pressure rings are used the oil consumption rises, because it cannot escape from the piston ring area sufficiently fast as more oil is fed to that area. When a new engine has been run on a particular viscosity oil it is good practice to stick to that viscosity. Any distant deviations either up or down may create increased oil consumption.

Invariably engine-makers specify the correct viscosity for their engines or give approval to proprietary brands. It saves a lot of trouble to accept their advice. All the big oil companies publish lists of cars and the lubricants recommended.

Bearing failures in these days are not often due to a faulty metal or bad oil if obtained from reputable suppliers, they are most likely caused by a restricted oil supply, through a choked feed pipe, thereby allowing the bearing to increase in temperature. The temperature may rise and then remain stationary, simply because there is insufficient oil flowing to preserve the normal temperature. At this higher temperature the life of the bearing is much reduced, and at still higher temperatures it may be exceedingly short. Apart from actual melting of the bearing metal most bearings ultimately fail through the development of fatigue cracks.

American engine builders have adopted a viscosity classification published by the Society of Automotive Engineers. It is well to stress the fact that this classification relates solely to viscosity and not to any other quality whatsoever. By this scheme a certain viscosity range is recommended, and the onus of selecting a sufficiently high quality oil is left with the owner of the car. For simplicity a number follows the letters S.A.E. to indicate the viscosity range.

Quenching of metals is the process of withdrawing heat from metal rapidly to obtain a required structure. The quenching medium serves no other purpose. The ancient practice of plunging a heated steel blade through a slave's thigh to harden it is an example of the needless suffering often caused by superstition. Even to-day superstition and want of knowledge sometimes enter into the choice of quenching media. The loss of heat is influenced by the shape and size of the object, the boiling-point of the fluid, and its viscosity. When hot metal is immersed in water vapour is immediately produced adjacent to the metal. Clearly this condition does not last long as the vapour and the water quickly mix. During these two phases cooling of the metal ensues, but at different rates. Finally cooling takes place in the liquid water by convection and conduction.

Vis. Saybolt Universal

S.A.E. No.	130° F. Min.	130° F. Max.	210° F. Min.	210° F. Max.
10	90	less than 120	—	—
20	120	,, ,, 185	—	—
30	185	,, ,, 255	—	—
40	255		—	less than 80
50			80	,, ,, 105
60			105	,, ,, 125
70			125	,, ,, 150

10 W 5,000 – 12,000 at 0° F.
20 W 10,000 – 48,000 at 0° F.

The aim of quenching is to produce a skin of hard metal, or an even hardness throughout the body of the metal. The operation should be so conducted to avoid distortion. Surface hardening is achieved by a rapid quench, consequently water is used. Oils are used when a more complete and slower quench is desired. Alloy steels are usually quenched moderately slowly to evade cracking and distortion.

Whale oil has long been regarded favourably as a quenching oil. It has a low viscosity and high flash point. But what a smell, particularly the cheaper grades. The supply position during the 1914 war encouraged an interest in mineral oils. At first there was a fear that they would introduce serious fire hazards. However, as time progressed they became more and more established as the metal industries learnt how to use them. To-day they are used in large quantities. The great advantage in them is that they can be supplied to any viscosity to meet individual needs. Some carbon steels need a fairly rapid quench, which is obtained by a low-viscosity oil; others a slower quench, in which event a more viscous oil is supplied, and tool steels which are still more slowly cooled prefer an oil having a viscosity of about 90 Redwood seconds at 140°F.

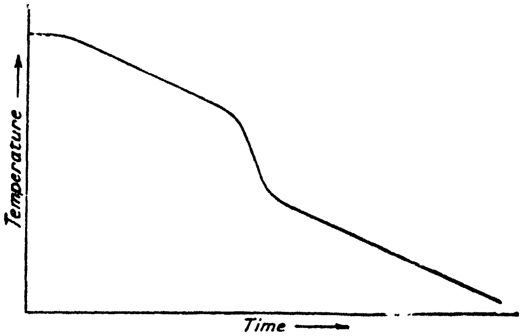


Fig. 39.—Diagrammatic Cooling Curve.

Many quenching baths are supplied with an oil cooler to maintain the oil within a temperature range, and to enable more quenchings to be done without heating the oil to too high a temperature.

Refrigerators rely upon the expansion of a gas under-pressure to lower the temperature. The gas may remain in the gaseous state or it may liquefy under pressure, but the principle is the same. From the aspect of lubrication, however, the two states are usually treated differently. When carbon dioxide or ammonia are employed they are invariably in the gaseous state, but sulphur dioxide, methyl chloride and freon are liquefied. Clearly if the gas is inert towards oil the worst it can do is to dissolve in the oil, but a liquid can be a selective solvent. Therefore when liquefied refrigerants are used it is essential that a lubricant shall be chosen which will not part with some of its constituents to the refrigerant. It will be remembered that in the Edeleanu refining process the mineral oil is treated with liquid sulphur dioxide to remove the aromatics. For sulphur dioxide refrigerators a suitable Edeleanu refined oil would be a natural choice, but not necessarily the only one.

A low pour point is generally chosen so that the oil will not freeze if it gets into the cold system. What the pour point shall be depends entirely upon the temperature it must withstand and what the risks are of it accumulating in the cold parts. For some refrigerators 15°F. is low enough, but for rapid fish freezing a pour point of —40°F. may be necessary. Low pour point is usually restricted to low viscosity oils, consequently refrigerator oils very rarely extend beyond the spindle oil class.

If lubricating oil from the compressor is admitted into the system it accumulates in the evaporator pipe system, and causes inefficient working by forming a coating over the inside of the pipes which affects the rate of heat transmission. To limit this the plant should have a separator vessel in the discharge pipe between the compressor and condenser. When a compressor is operating a dry compression the discharged gas is hot. In this case the separator is some distance away to allow the gas to cool, and any oil vapour to condense, and atomised oil to coalesce. The separated oil is removed and the gas proceeds on its journey. Some care is necessary if ammonia under pressure is liberated to atmosphere, therefore a second container is often attached to the suction side of the compressor to collect ammonia liberated from the oil.

Sewing Machines are frequently regarded as household equipment, but these small machines are almost insignificant when compared with the enormous number of sewing machines used in dozens of industries. Each of these industries have individual needs. The household machine simply needs a pure mineral oil of pale colour, free from fatty oil, and of low viscosity. An essential characteristic is that it shall not gum when left for long periods; indeed, this characteristic is needed for all sewing machines. In the corset-making industry high-speed machines are employed which would spray oil on to the fabric if the oil were too light and fed too liberally. After all the care which is exercised occasional spots of oil do go astray. Solvent spotting out of oil spots can be used to a limited extent, but it is better to use a water white oil which will remain unobserved when on the fabric. Garments which are washed before entering the shops are sewn with machines lubricated with oil which is easily emulsified with ordinary detergents. Fatty oils or fatty acids are blended with the mineral oil to assist in forming an easily removable emulsion. The use of wetting agents has not progressed very far yet in lubricants for this class of work. They are mainly applied to the yarn in the textile industries.

In the hosiery trade where vests and the like are made for women's underwear very fast machines are commonly employed, often making 5,000 stitches per minute. Amber oils created much staining of the garments, consequently white oils were tried, but not entirely with success. Exposure of the article to sunlight in shop windows caused oil spots to gild. The efforts to select oils free from gilding tendency were largely rewarded with success, but at a price which would not compete with oils containing fatty oils and acids. As these commodities are washed and got up before being sold, a visible oil spot is an advantage to the launderess who can see if it has been removed.

High-speed machines are all lubricated with lubricants chosen from the spindle oil class. Heavier machines, such as those employed in the boot and shoe industry, generally want an oil of somewhat higher viscosity.

Steam Engines. As inquiries are often made about the lubrication of steam engines many years ago it may interest readers to know something of the development of these engines. It was in 1685 that Papin of France produced an engine based on the fact that when cold water is applied to a vessel containing steam a vacuum results. Savery immediately applied the idea to raising water. But it was Newcombe of Dartmouth, in 1705, who constructed the first steam engine properly called. James Watt introduced many improvements, especially the separate condensing chamber in place of admitting the injected water into the cylinder which tends to lower the temperature of the cylinder walls. He specified that the cylinder should be kept as hot as the steam which enters it. He also invented mechanism for automatically opening and closing the valves, introduced the use of steam above atmospheric pressure, and discontinued the use of atmospheric pressure alone by making use of the expansion of the steam for doing work on the piston. Watt's first engine was built in 1768. The so-called high-pressure engine using steam at 3–4 atmospheres was designed by Oliver Evans in America, 1786–1801. With high-pressure steam the advantage of expansion is very great. Steam is admitted at high pressure for a short period of the piston stroke only, and then allowed to expand down to the end of the stroke, losing heat thereby by doing work. If the expansion is carried too far the cooling becomes so great as to condense part of the steam. To prevent waste from this cause the expansion is carried out in two or more cylinders of different capacities. Engines on this principle are called compound if they have two cylinders, triple expansion with three cylinders, and quadruple expansion with four cylinders.

The earliest attempt at a compound engine was made by Hornblower in 1781. Woolf took out a patent in 1804 for a two-cylinder high-pressure engine with condenser, together with water tube boiler. In 1850 Elder brought the compound engine into successful use for machine purposes. Then in 1881 electric lighting came on the scene. Slow-running engines geared up with belting were not sufficiently well governed to prevent light flicker, consequently a quick revolution engine was introduced by George Bellis. He introduced forced feed lubrication to all parts, and patented the invention in 1890.

About 1880 the steam engine encountered a rival in the gas engine. Sir Frederick Bramwell in 1881 at the British Association suggested that the steam motor would be a museum curiosity in fifty years' time; in fact he left money to be devoted by a distinguished man to deal with prime movers in 1921. The lecture was duly delivered by Sir Alfred Ewing, who said, "steam is neither dead nor dying." In the meantime Sir Charles Parsons and others had developed the steam turbine.

The lubrication of the early engines was no ordeal, in fact tallow was commonly used, rape oil or shale oil or both was available for bearings. By the time that Bellis made the big advance mineral oils of good quality were on the market. It is probably true to say that a big improvement in cylinder oils was prompted by the adoption of superheated steam early this century. Nowadays cylinder lubrication is pretty well standardised to three different viscosity mineral oils for dry steam at different temperatures, and where the exhaust steam is condensed and used again. Boiler water contaminated with fatty oils or fatty acids is liable to create trouble in the boiler.

Steam Turbines. Guy and Smith (Gen. Dis., I.M.E., 1937) collected a statement of current turbine journal bearing practice through the co-operation of the six principal makers in this country. Bearing pressures are only between 57 and 150 lb. per sq. in. of projected area, but in particular cases they may be as low as 27 lb. per sq. in. or as high as 200 lb. Surface speeds of journals up to 157 ft. per sec. are commonly used, whilst 177 ft. per sec. represent the maximum in current practice. The diametral clearance below 0·001 inch per inch to 0·003 inch per inch. With a clearance below 0·001 inch per inch undue heating may occur, and when it is above 0·003 inch per inch vibration is experienced.

The various makers have their own formula for calculating the oil quantity with which the bearing is to be supplied. For a bearing 10 inches in diameter and 10 inches long running at 3,000 r.p.m. assessments range from 11·3 to 26·7 gal. per min., while for a bearing 20 inches in diameter and 20 inches long running at 1,500 r.p.m. the assessments range from 45 to 82 gal. per min. There are very definite limits to the permissible reduction in oil quantity for a particular high-speed bearing. As the quantity is reduced a point is reached at which vibration begins as a result of some instability in the oil film, and the temperature along the bearing increases, also aeration of the oil increases. For these reasons the quantity of oil supplied to a bearing must be very considerably greater than the minimum with which the bearing can be run.

In addition to lubricating the bearings, oil is used to carry away the heat, consequently a generous flow must be maintained. The importance of the effective disposal of this heat will be appreciated when it is realised that for a large modern turbo-generator the heat to be extracted from the oil is of the order of 2,000,000 B.T.U. per hour. All this heat has to be extracted before the oil is re-circulated to absorb more heat from the bearings. Oil coolers are therefore incorporated in the lubricating system. To allow adequate time for the oil to be cooled, freed from air bubbles, and some settlement, one change of oil through the system every 6 to 8 minutes is generally allowed in large modern machines. This involves large oil capacities of the order of 500 gallons for a 10,000 kw. machine to 2,500 gallons for a 50,000 kw. machine.

The practice of filling a new turbine with a flushing oil, prior to the main charge, is growing. It has the advantage of removing all the moulding sand from the castings, all the bits of loose metal from machinery, fluff from cotton wipers, etc. After a few weeks of running it is withdrawn, filtered and perhaps earthed to improve its demulsification value, and used again in another turbine, which might be a new one or an old one from which the oil has been withdrawn. The flushing oil removes the remaining oil in odd pockets and the loose sludge. Flushing of old turbines occasionally is recommended. After flushing the main new charge of oil is put into circulation.

Turbine oils are generally of low viscosity, about 70 to 100 seconds Redwood at 140°F. The very light loading on the bearing and high rotor speeds only demand a low viscosity. For many years specially selected Penna oils were chosen for high-class work, but to-day they find competition from solvent refined oils. Turbine oils have rightly been regarded as a distinctive class and have claimed a high price. The reason being that they are made from selected crudes which respond to a treatment which will produce a lubricant of low demulsification, low oxidation, low acid generation, and low volatility. Solvent refining has brought on to the market oils of these characteristics, but some care is necessary in selecting them because some of them are prone to rapid acid development in use. Fortunately acid development can be checked by the addition of chemical inhibiters. The two which are widely used in this country are tertiary butyl cresol and β-naphthol. Their activity is so great that it is only necessary to use quantities of the order of 0·1 per cent. Tertiary butyl cresol has been found effective in white oils, Penna neutrals, solvent oils, mid/Continent oils and even in some used oils. As it is a liquid it can be added to the oil already in the turbine. This is particularly useful if it is desirable to add a supplementary quantity to the inhibited oil in service.

The formation of acids in turbine oils has long been a controversial subject. It arose shortly after the 1914 war when there was a mild epidemic of pitted bearings. Then it was found that when the free acidity of the oil was below 0·8 mg. KOH per gram of oil, no pitting resulted, but above that value pitting occurred. For safety 0·8 was put as the maximum safe figure. Safety was secured, but a lot of good oil was discarded as a result. Slowly the figure was permitted to rise to 1·9. There are many cases on record of an acidity up to 4·0 where no trouble has ensued. Some power-station engineers alarm at an acidity of 0·4. Of course, these men are responsible for big sets, and continuous running in important areas, and feel that hazards should be reduced to the minimum.

Recent developments in power stations have introduced a substantial fire hazard. Probably fires which have resulted have emphasised the hazard sufficiently. Steam is often conveyed through pipes at a temperature in excess of the ignition temperature of oil, consequently if oil is allowed to spray upon one of these steam pipes, ignition may occur and a nasty fire result. A surface temperature of 560° F. is sufficient to ignite a turbine oil, although temperatures up to 750° are known to be safe. Lagging would naturally appear to provide the necessary protection, but this is not necessarily so. Oil may penetrate it through a crack or a joint. Barclay (Gen. Dis., I.M.E., 1937) allowed oil to drip on a superheated steam pipe and collected the products. The original oil had a flash point of 400° F. and the condensed vapours 174°.

For geared turbines more viscous oils are usually employed, mainly to suit the needs of the gears.

Some sludge formation always occurs in turbine oils, therefore centrifuges are now regarded as an integral part of a turbine equipment. Should it be decided to examine a sample of sludge, bear in mind that it may not be sludge at all, but viscous oil emulsion. Should much emulsion form, an effort should be made to stop the escape of water into the oil. A little water is a common impurity, but if it is drawn off at regular intervals little trouble is encountered. Turbines which make much water are a source of trouble.

Insufficient attention has been given to the oil coolers in the past. During the passage of the heated oil through the cooler it deposits sludge and more sludge until much of the space between the cooling pipes becomes choked with solid material. The cleaning of the coolers was a horrible job. The nest of pipes was withdrawn, and the sludge removed by any mechanical device which could be conceived, which was frequently a piece of wire and a water jet. Now all that inefficient toil has been replaced by solvent extraction. Two methods are in vogue. One consists of vaporising trichlorethylene into the cooler from a boiler, the other of pouring a gallon or two of tetrahydronaphthalene into the cooler and then injecting steam. These solvents remove the sludge without dismantling. The simplicity of these methods must encourage engineers to keep the oil coolers in a proper state of efficiency. Both methods are protected by patent rights.

Tempering of metals follows quenching to release internal stresses and other unstable conditions developed. It is always done at a temperature lower than that from which the metal is quenched. Tempering consists of maintaining the metal at a predetermined temperature for a period. Sometimes it is done in an oven, and sometimes in heated oil. When oil is used particular attention is given to its flash point, degree of vaporisation and sludge formation. A good cylinder oil having a flash point above 500°F. is usually satisfactory.

Thermostats find a wide application in many industries, and their temperature range is extensive. In a pump-circulating system pumping losses can be kept to a minimum by employing the lowest viscosity oil which it is safe to use. The safety factor is controlled by the flash point of the oil and the working temperature. As avoidance of fire hazard is far more important than pumping losses, first thought should be given to flash point, but not only flash point if the oil temperature is high. Cracking of the oil at high temperatures will give rise to lower flash point hydrocarbons, hence attention must be given to oil cracking temperature. Although in normal operation cracking may not occur, the hazard may easily arise if carbonisation results and thereby excessive local heating. As oil would only be used for temperatures above 100° C. any inconvenience caused by high viscosity could hardly develop, so it is recommended that a low pour point filtered cylinder oil should be used. Such an oil has a flash point of about 500° F., is very resistant to oxidation, is reasonably stable, and is not too viscous to stir at atmospheric temperature. Thinner oils are used satisfactorily, perhaps without much hazard. But is an oil fire worth risking?

When temperatures above 450° F. are required an oil with a flash point of over 600° F. is used. There are critics who hold that this type of oil is liable to crack before the flash point is reached. No doubt the oil supplier will be able to give any necessary advice to a purchaser.

Transformer oil and switch oil is well specified in B.S.S. 148. In this country B.S.S. 148 is accepted hardly without comment. Two oils are specified, Grades A and B. The basic differences between the two oils is their respective sludge value. Grade A was intended for high temperature transformers, and Grade B for lower temperatures. Behind this publication lies a vast volume of research made for the British Electrical and Allied Industries Research Association. The exigencies of war have enforced the suspension of Grade A, therefore it will be interesting to see the results obtained by the extended use of Grade B. War-time conditions have also called for a slight increase in the sludge value of the oil.

The use of mineral oil for electrical insulating purposes is often believed too date back to 1906, when Moody was granted a patent. Digby and Mellis, in 1910, read a paper before the Institution of Electrical Engineers defending the use of mineral oil, and Duckham (*Electrical Times*, 1910) made suggestions as to the cause of the formation of solid deposits which occur in transformers when mineral oils are used. Michie studied these deposits, and suggested the sludge test in 1913. This test has been standardised and adopted in this country. The test was designed to measure the propensity of an oil to form sludge in service. The disadvantage of sludge in a transformer is that it interferes with heat dissipation from the windings. Of course, oil is primarily required for cooling the windings, but it must also be capable of being an electrical insulator, or, in other words, have a high electrical breakdown value.

The oil shall have a sufficiently low viscosity to circulate freely, low pour point to guard against freezing, refined to a specified sludge value to obviate sludge formation, and freed from moisture and fibre to raise the B.D.V. These are the main requirements.

The B.D.V. is not difficult to attain. A good centrifuge under proper supervision will remove the moisture and fibre and raise the B.D.V. to 50,000 volts or even higher. To maintain this value is the real problem. Very small quantities of moisture and fibre will reduce it considerably, therefore great care must be taken in ensuring that the storage tanks, barrels and drums are capable of excluding contamination. The technique has been evolved over a long period of years, and much attention has been given by the filter makers. The measurement of B.D.V. was studied by Everest in 1921, who established that needle point electrodes give uniform B.D.V. because of their insensitivity to the presence of contaminating impurities. He concluded that spheres are the electrodes which are the most free from criticism.

The B.D.V. of oils is useful in detecting small amounts of water in oils generally, especially refrigerator oils used in conjunction with SO_2. Pure water has a high B.D.V., so water alone may not reduce the B.D.V. very seriously, but immediately it comes in contact with impurities and fibre a reduction occurs.

Sludging of oils has been the subject of detailed research and almost endless discussion between chemists and engineers throughout the world, and still it would go on if the war had not intervened. All the efforts to arrive at international unity have failed, in fact there seems to have been little inclination for one national to give way to another. In this country we stick to the Michie sludge test; in Switzerland Brown Boveri heat the oil for 300 hours at 115° C. in the presence of copper and cotton. At the end of the test the reduction in the tensile strength of the cotton is determined. The Kissling test is adopted in Germany. It consists of blowing oxygen into the oil at 120° C. for 70 hours, then extracting with sodium hydroxide, acidifying the extract with hydrochloric acid, and weighing the separated organic acids. The A.S.E.A. blow with oxygen at 110° C. in the presence of iron and copper, and maintain the oil under 10,000 volts. The Snyder test in the U.S.A. takes the time for the first appearance of sludge when air is passed over 500 ml. of oil maintained at 120° C.

To attempt to uphold any of these individual tests is sure to invite criticism. Out of all the conflict of opinions on the actual tests the fact stands out that transformers are used the world over and the experts in the different countries are satisfied with their choice, and the petroleum industry as a whole supplies the goods.

Much of the conflict can be traced to the battle over sludge and acid formation. In Switzerland and Germany the cotton windings are exposed to the oil, therefore it is natural that some concern is evidenced about the production of acid and its behaviour towards cotton. As the cotton is often varnished in this country we are less anxious about acid and more fussy about sludge. In Sweden the transformer makers believe that the test is made more practical by introducing an electrical stress. How repeatable and scientific the several tests are is entirely another phase of the subject, the probability is that they are all full of weaknesses and subject to correction. Grade A is undoubtedly more free from sludge than Grade B, but it produces more free acid. During recent years the quantity of Grade B used in this country has increased, while Grade A has diminished. Now, during the war, only Grade B is available.

The growing interest in anti-oxidants in other oils has not extended appreciably to transformer oils, but it will come—it must come whatever the opposition. The difficulty at the moment is that anti-oxidants may be added which will get an oil through the sludge test and into use without evidence that it will withstand the oxidising life in the transformer. As in other cases where chemical addition agents are used, some system of approval must appear. It has been done in hypoid oils. Anti-oxidants are already in use and are behaving as well as was anticipated.

When should an oil be abandoned is always a great difficulty. No one has been sufficiently bold to lay down rules, but suggestions have been made. Probably an examination of the windings gives the best clue. Another vexed question is what to do with transformers which need a new change of oil. Some engineers hold that the paper insulation must have suffered damage and should be replaced. Any attempt at washing down with solvents should be avoided. In spite of these fears washing has been undertaken on a generous scale during the last year or two, so far without disaster. It is perhaps too early to push its use fearlessly. Before embarking upon solvent washing the advocates must convince themselves of the suitability of the fluid.

Fire risks are often associated with flash point. B.S.S. 148 does not specify a high flash point, nor do American authorities. When B.S.S. 148 was being revised a few years ago not one single case of fire could be produced which was attributable to the flash point of the oil. Accidental fires will always happen. Most fires have been traced to breakdown of the insulated covering of the wires and the arcing which has followed. When this happens hydrogen is liberated from the oil and is ignited. In switches fires have been started by dirt getting between the contacts and allowing small arcs to form, pitting of the metal takes place and the intensity of the arc increases.

Wire drawing has not emerged from its age of mystery. The skilled wire drawer serves a long period of training, and at the end is usually free to use what lubricant pleases him best. Wire drawing is full of difficulties, and probably will remain so until sufficient fundamental work has been done to explain the plastic flow of the metal, the reasons for variation in diameter, causes of surface cracks and changes in tensile strength. Any wire drawer will readily admit that lubrication plays an important part, but he cannot go further than stating certain things are good and other things are bad.

In 1650 a revolutionary discovery is alleged to have been made by a German wire drawer at Altona. He failed to draw some steel wire, so he threw it out of the window. A few days later the owner of the factory found it, and demanded that it must be drawn. To their amazement it drew exceptionally easily. Inquiry discovered the fact that the wire had lain in wet ground adjacent to an earth lavatory, and that it had acquired a surface of scum. The secret was carefully preserved for about 100 years, although the wives and children of the workers went daily to the works bearing a yoke, one bucket contained the man's lunch and the other the family contribution to the art of sull coating. About 1750 it was found that sour beer would give a sull coating. Now it is known that brewers yeast has a similar effect. How these organic bodies react is not known.

For the drawing of iron wire it is customary to give it a coating of lime. Then it may be drawn wet or dry. Wet drawing consists of immersing the coil of wire in an emulsion rich in fatty oil, and drawing the wetted wire through the die. Particles of anhydrous sodium soap is allowed to rub against the wire as it passes to the die in dry drawing. How lime came to be used seems obscure. Some people state that it was used, and still is, to neutralise the acid after pickling. Against this belief there is evidence that lime was used before acid cleaning was introduced. What the effect of lime is does not appear to have been published.

Bees-wax, copper oleate, ceresin have been suggested as wire-drawing lubricants. It is stated that when the temperature of the die is above the melting-point of these substances the coefficient of friction rises to that of the fluid oils at the same temperature. Consequently, to be effective they must enter the die in solid form to be useful. One would have thought that the temperature in the zone of maximum pressure in the die would be sufficiently high to melt any of these comparatively low melting-point bodies under commercial wire-drawing conditions. Solid lubricants like graphite and talc are not favoured. The problem might appear to be one for extreme pressure lubrication, but so far this has not been the case.

Wire Ropes are used for a multiplicity of purposes, and have replaced chains to a considerable extent for lifting and haulage. For some operations it would be inconvenient to apply any lubricant to them once they are installed. For other uses it would seem proper to oil a rope to enable the individial wires to move over each other with the minimum of friction. It would also appear to be proper to apply oil to the outside of the rope to protect it against atmospheric corrosion. A close examination of cross-sections of industrial wire ropes will very quickly reveal that they are of very complex structure, and often so compact that it would be difficult to induce an oil to penetrate it except by complete immersion, and then only by removing the air under a vacuum and subsequent application of pressure. The external application of oil to a closely knit rope can only be regarded as a surface dressing. With a clean rope some oil may penetrate, and if the application is made sufficiently often it may penetrate still farther. But it may not, and as there is no means of determining the depth of penetration without cutting the rope only an assumption can be made. As many other assumptions are allowed, this one need not cause dismay. Within the rope cracks may occur, local wear develop, fatigue cracks grow, and so on, none of which can be foretold, consequently a wire rope is allotted a span of life based upon a probable safety factor.

A thin oil applied to the surface will have a better chance of penetrating than a viscous oil, but whether it will provide adequate lubrication under the heavy flexing of the rope and sufficient protection against corrosion is a problem to be answered. Furthermore, as wear takes place particles of iron are being churned into an abrasive paste with the oil in the interstitial spaces the lubricant should be sufficiently viscous to reduce the abrasion. On the external parts of the rope sand and dust will collect and be held. A thick oil will not penetrate, but will make a protective cover to exclude dirt and moisture and corrosive gases.

Wire ropes invariably contain a hemp core. Before the wire is spun around the core it is well oiled, and so serves as a reservoir for the lubricant. During the building of the rope a further quantity of lubricant is applied The lubricant varies from thick oil to petroleum jelly.

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